(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
10 November 2005 (10.11.2005)

PCT

(10) International Publication Number
WO 2005/104756 A2

(51) International Patent Classification: Not classified

(21) International Application Number: PCT/US2005/014449

(22) International Filing Date: 27 April 2005 (27.04.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/565,604 27 April 2004 (27.04.2004) US

(71) Applicant (*for all designated States except US*): **THE BOARD OF TRUSTEES OF THE UNIVERSITY OF ILLINOIS** [US/US]; 352 Henry Administration Building, 506 S. Wright Street, Urbana, IL 61801 (US).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): **ROGERS, John, A.** [US/US]; 4305 Brittany Trail Drive, Champaign, IL 61822 (US). **MENARD, Etienne** [FR/US]; 705 W. Oregon, Urbana, IL 61801 (US).

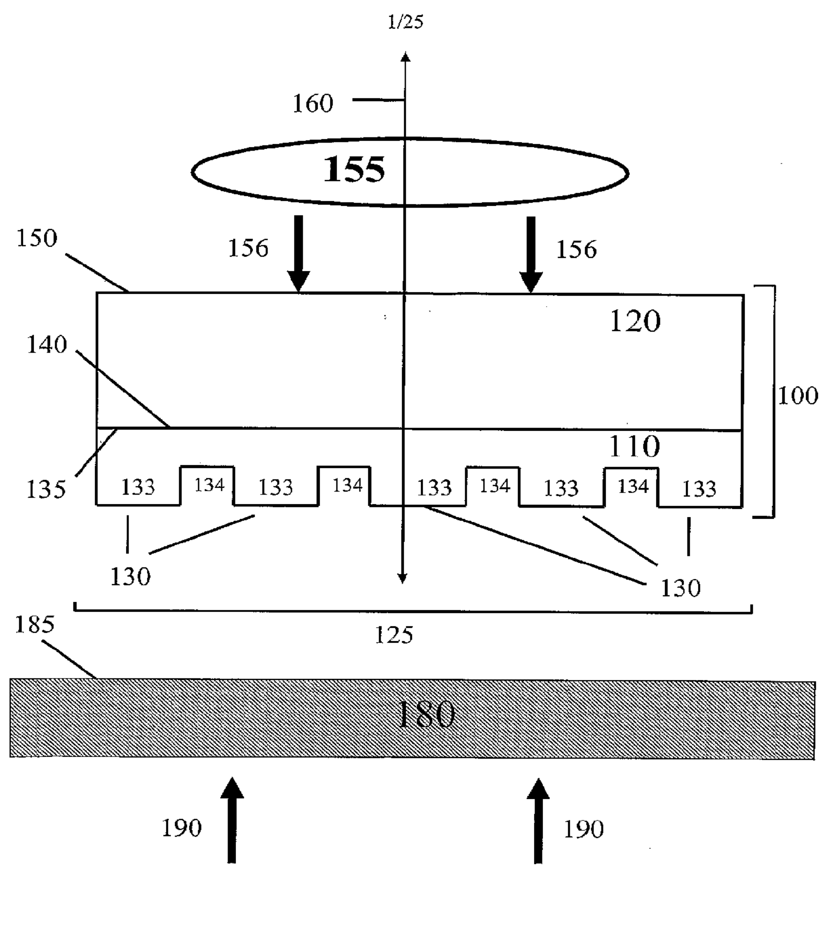
(74) Agents: **BARONE, Stephen, B.** et al.; 4875 Pearl East Circle, Suite 200, Boulder, CO 80301 (US).

(81) **Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH,

[Continued on next page]

(54) **Title:** COMPOSITE PATTERNING DEVICES FOR SOFT LITHOGRAPHY



(57) Abstract: The present invention provides methods, devices and device components for fabricating patterns on substrate surfaces, particularly patterns comprising structures having microsized and/or nanosized features of selected lengths in one, two or three dimensions. The present invention provides composite patterning devices comprising a plurality of polymer layers each having selected mechanical properties, such as Young's Modulus and flexural rigidity, selected physical dimensions, such as thickness, surface area and relief pattern dimensions, and selected thermal properties, such as coefficients of thermal expansion, to provide high resolution patterning on a variety of substrate surfaces and surface morphologies.

WO 2005/104756 A2

GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

PCT/US05/14449

COMPOSITE PATTERNING DEVICES FOR SOFT LITHOGRAPHY

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Patent Application 60/565,604, filed April 27, 2004, which is hereby incorporated by reference in its entirety to the extent not inconsistent with the disclosure herein.

BACKGROUND OF INVENTION

[0002] The design and fabrication of micrometer sized structures and devices have had an enormous impact on a number of important technologies including microelectronics, optoelectronics, microfluidics and microsensing. The ability to make micro-sized electronic devices, for example, has revolutionized the electronics field resulting in faster and higher performing electronic components requiring substantially less power. As these technologies continue to rapidly develop, it has become increasingly apparent that additional gains are to be realized by developing the ability to manipulate and organize matter on the scale of nanometers. Advances in nanoscience and technology promise to dramatically impact many areas of technology ranging from materials science to applied engineering to biotechnology.

[0003] Fabrication of devices having nanoscale dimensions is not merely a natural extension of the concept of miniaturization, but a fundamentally different regime in which physical and chemical behavior deviates from larger scale systems. For example, the behavior of nanoscale assemblies of many materials is greatly influenced by their large interfacial volume fractions and quantum mechanical effects due to electronic confinement. The ability to make structures having well-defined features on the scale of nanometers has opened up the possibility of making devices based on properties and processes only occurring at nanometer dimensions, such single-electron tunneling, Coulomb blockage and quantum size effect. The development of commercially practical methods of fabricating sub-micrometer sized structures from a wide range of materials, however, is critical to continued advances in nanoscience and technology.

[0004] Photolithography is currently the most prevalent method of microfabrication, and nearly all integrated electronic circuits are made using this technique. In conventional projection mode photolithography, an optical image corresponding to a selected two dimensional pattern is generated using a photomask. The image is optically reduced and projected onto a thin film of photoresist spin coated onto a substrate. Alternatively, in Direct Write to Wafer photolithographic techniques, a photoresist is directly exposed to laser light, an electron beam or ion beam without the use of a photomask. Interaction between light, electrons and/or ions and molecules comprising the photoresist chemically alters selected regions of the photoresist in a manner enabling fabrication of structures having well defined physical dimensions. Photolithography is exceptionally well suited for generating two-dimensional distributions of features on flat surfaces. In addition, photolithography is capable of generating more complex three dimensional distributions of features on flat surfaces using additive fabrication methods involving formation of multilayer stacks.

[0005] Recent advances in photolithography have extended its applicability to the manufacture of structures having dimensions in the submicron range. For example, nanolithographic techniques, such as deep UV projection mode lithography, soft X-ray lithography, electron beam lithography and scanning probe methods, have been successfully employed to fabricate structures with features on the order of 10s to 100s of nanometers. Although nanolithography provides viable methods of fabricating structures and devices having nanometer dimensions, these methods have certain limitations that hinder their practical integration into commercial methods providing low cost, high volume processing of nanomaterials. First, nanolithographic methods require elaborate and expensive steppers or writing tools to direct light, electrons and/or ions onto photoresist surfaces. Second, these methods are limited to patterning a very narrow range of specialized materials, and are poorly suited for introducing specific chemical functionalities into nanostructures. Third, conventional nanolithography is limited to fabrication of nanosized features on small areas of ultra-flat, rigid surfaces of inorganic substrates and, thus is less compatible with patterning on glass, carbon and plastic surfaces. Finally, fabrication of nanostructures comprising features having selectable lengths in three dimensions is difficult due to the limited depth of focus provided by

PCT/US05/14449

nanolithographic methods, and typically requires labor intensive repetitive processing of multilayers.

[0006] The practical limitations of photolithographic methods as applied to nanofabrication have stimulated substantial interest in developing alternative, non-photolithographic methods for fabricating nanoscale structures. In recent years, new techniques based on molding, contact printing and embossing collectively referred to as soft lithography have been developed,. These techniques use a conformable patterning device, such as a stamp, a mold or mask, having a transfer surface comprising a well defined relief pattern. Microsized and nanosized structures are formed by material processing involving conformal contact on a molecular scale between the substrate and the transfer surface of the patterning device. Patterning devices used in soft lithography typically comprise elastomeric materials, such as poly(dimethylsiloxane) (PDMS), and are commonly prepared by casting prepolymers against masters generated using conventional photolithography. The mechanical characteristics of the patterning devices are critical to the fabrication of mechanically robust patterns of transferred materials having good fidelity and placement accuracy.

[0007] Soft lithographic methods capable of generating microsized and/or nanosized structures include nanotransfer printing, microtransfer molding, replica molding, micromolding in capillaries, near field phase shift lithography, and solvent assisted micromolding. Conventional soft lithographic contact printing methods, for example, have been used to generate patterns of self assembled monolayers of gold having features with lateral dimensions as small as about 250 nm. Structures generated by soft lithography have been integrated into a range of devices including diodes, photoluminescent porous silican pixels, organic light emitting diodes and thin-film transistors. Other applications of this technology generally include the fabrication flexible electronic components, microelectromechanical systems, microanalytical systems and nanophotonic systems.

[0008] Soft lithographic methods for making nanostructures provide a number of benefits important to fabricating nanoscale structures and devices. First, these methods are compatible with a wide range of substrates, such as flexible plastics,

carbonaceous materials, ceramics, silicon and glasses, and tolerate a wide range of transfer materials, including metals, complex organic compounds, colloidal materials, suspensions, biological molecules, cells and salt solutions. Second, soft lithography is capable of generating features of transferred materials both on flat and contoured surfaces, and is capable of rapidly and effectively patterning large areas of substrate. Third, soft lithographic techniques are well-suited for nanofabrication of three dimensional structures characterized by features having selectably adjustable lengths in three-dimensions. Finally, soft lithography provides low cost methods which are potentially adaptable to existing commercial printing and molding techniques.

[0009] Although conventional PDMS patterning devices are capable of establishing reproducible conformal contact with a variety of substrate materials and surface contours, use of these devices for making features in the sub-100 nm range are subject to problems associated with pressure induced deformations due to the low modulus (3MPa) and high compressibility (2.0 N/mm^2) of conventional single layer PDMS stamps and molds. First, at aspect ratios less than about 0.3, conventional PDMS patterning devices having wide and shallow relief features tend to collapse upon contact with the surface of the substrate. Second, adjacent features of conventional single layer PDMS patterning devices having closely spaced (< about 200 nm), narrow (< about 200 nm) structures tend to collapse together upon contact with a substrate surface. Finally, conventional PDMS stamps are susceptible to rounding of sharp corners in transferred patterns when a stamp is released from a substrate due to surface tension. The combined effect of these problems is to introduce unwanted distortions into the patterns of materials transferred to a substrate. To minimizing pattern distortions caused by conventional single layer PDMS patterning devices, composite patterning devices comprising multilayer stamps and molds have been examined as a means of generating structures having dimensions less than 100 nm.

[0010] Michel and coauthors report microcontact printing methods using a composite stamp composed of a thin bendable layer of metal, glass or polymer attached to an elastomeric layer having a transfer surface with a relief pattern. [Michel et al. Printing Meets Lithography: Soft Approaches to High Resolution

PCT/US05/14449
Patterning, IBM J. Res. & Dev., Vol. 45, No. 5, pgs 697 – 719 (Sept. 2001). These authors also describe a composite stamp design consisting of a rigid supporting layer and a polymer backing layer comprising a first soft polymer layer attached to a second harder layer having a transfer surface with a relief pattern. The authors report that the disclosed composite stamp designs are useful for "large area, high-resolution printing applications with feature sizes as small as 80 nm."

[0011] Odom and coauthors disclose a composite, two layer stamp design consisting of a thick (≈ 3 mm) backing layer of 184 PDMS attached to a thin (30 – 40 microns), layer of *h*-PDMS having a transfer surface with relief patterns . [Odem et al., Langmuir, Vol. 18, pgs 5314 – 5320 (2002). The composite stamp was used in this study to mold features having dimensions on the order of 100 nm using soft lithography phase shifting photolithography methods. The authors report that the disclosed composite stamp exhibits increase mechanical stability resulting in a reduction in sidewall buckling and sagging with respect to conventional low modulus, single layer PDMS stamps.

[0012] Although use of conventional composite stamps and molds have improved to some degree the capabilities of soft lithography methods for generating features having dimensions in the sub-100 nm range, these techniques remain susceptible to a number of problems which hinder there effective commercial application for high throughput fabrication of micro-scale and nanoscale devices. First, some conventional composite stamp and mold designs have limited flexibility and, thus, do not make good conformal contact with contoured or rough surfaces. Second, relief patterns of conventional, multimaterial PDMS stamps are susceptible to undesirable shrinkage during thermal or ultraviolet curing, which distort the relief patterns on their transfer surfaces. Third, use of conventional composite stamps comprising multilayers having different thermal expansion coefficients can result in distortions in relief patterns and curvature of their transfer surfaces induced by changes in temperature. Fourth, use of stiff and/or brittle backing layers, such as glass and some metal layers, prevents easy incorporation of conventional composite stamps into preexisting commercial printer configurations, such as rolled and flexographic printer configurations. Finally, use of composite stamps having transfer surfaces comprising high modulus elastomeric materials impede formation

of conformal contact between a transfer surface and a substrate surface necessary for high fidelity patterning.

[0013] It will be appreciated from the foregoing that there is currently a need in the art for methods and devices for fabricating high resolution patterns of structures having features on the scale of 10s to 100s of nanometers. Specifically, soft lithography methods and patterning devices are needed which are capable of fabricating patterns of nanoscale structures having high fidelity, good mechanical robustness and good placement accuracy. In addition, patterning devices are needed that minimize pattern distortions, for example by reducing relief pattern shrinkage during thermal or ultraviolet curing and/or minimizing temperature induced distortions as compared to conventional patterning devices. Finally, soft lithography methods and devices are needed that are compatible with and can be easily integrated into preexisting high speed commercial printing and molding systems.

SUMMARY OF THE INVENTION

[0014] The present invention provides methods, devices and device components for fabricating patterns on substrate surfaces, particularly patterns comprising structures having microsized and/or nanosized features of selected lengths in one, two or three dimensions. Specifically, the present invention provides stamps, molds and photomasks used in soft lithography fabrication methods for generating high resolution patterns of structures on flat and contoured surfaces, including surfaces having a large radius of curvature on a wide variety of substrates, including flexible plastic substrates. It is an object of the present invention to provide methods and devices for fabricating three-dimensional structures having well defined physical dimensions, particularly structures comprising well defined features having physical dimensions on the order of 10s of nanometers to 1000s of nanometers. It is another object of the present invention to provide methods, devices and device components for fabricating patterns of structures characterized by high fidelity over large substrate surface areas and good placement accuracy. It is further an object of the present invention to provide composite patterning devices which exhibit better thermal stability and resistance to curing induced pattern distortion than conventional single layer or multilayer stamps, molds and photomasks. It is another

PCT/US05/14449

object of the present invention to provide soft lithography methods, devices and device components that are compatible with existing high speed commercial printing, molding and embossing techniques, devices and systems.

[0015] In one aspect, the present invention provides patterning devices comprising a plurality of polymer layers each having selected mechanical properties, such as Young's Modulus and flexural rigidity, selected physical dimensions, such as thickness, surface area and relief pattern dimensions, and selected thermal properties, such as coefficients of thermal expansion, to provide high resolution patterning on a variety of substrate surfaces and surface morphologies. Patterning devices of this aspect of the present invention include multilayer polymer stamps, molds and photomasks useful for a variety of soft lithographic patterning applications including contact printing, molding and optical patterning. In one embodiment, discrete polymer layers having different mechanical properties, physical dimensions and thermal properties are combined and/or matched to provide patterning devices having cumulative mechanical and thermal properties providing enhanced pattern resolution and fidelity, and improved thermal stability over conventional soft lithography devices. In addition, patterning devices of the present invention comprising a combination of discrete polymer layers tolerate a wide variety of device configurations, positions and orientations without fracture which make them more easily integrated into existing commercial printing, molding and optical patterning systems than conventional single layer or multiple layer stamps, molds and photomasks.

[0016] In one embodiment, the present invention provides a composite patterning comprising a first polymer layer having a low Young's modulus and a second polymer layer having a high Young's modulus. The first polymer layer comprises a selected three-dimensional relief pattern having at least one contact surface disposed thereon and has an internal surface opposite the contact surface. The second polymer layer has an external surface and an internal surface. First and second polymer layers are arranged such that a force applied to the external surface of the second polymer layer is transmitted to the first polymer layer. For example, first and second polymer layers may be arranged such that a force applied to the external surface of the second layer is transmitted to at least a portion

of the contact surface(s) of the first polymer layer. In an embodiment, the internal surface of the first polymer layer is operationally coupled to the internal surface of the second polymer layer. For example, the internal surface of the first polymer layer may be in physical contact with the internal surface of the second polymer layer. Alternatively, the first polymer layer and the second polymer layer may be connected by one or more connecting layers, such as thin metal layers, polymer layers or ceramic layers, positioned between the internal surface of the first polymer layer and the internal surface of the second polymer layer.

[0017] Composite patterning devices of this aspect of the present invention are capable of establishing conformal contact between at least a portion of the contact surface(s) of the first polymer layer and the substrate surface undergoing patterning. Optionally, the second polymer layer may be operationally coupled to an actuator, such as a stamping, printing or molding device, capable of providing an external force to the external side of the second polymer layer so as to bring the patterning device into conformal contact with the substrate surface undergoing patterning. Optionally, the substrate may be operationally coupled to an actuator, capable of bringing the substrate into conformal contact with the patterning device.

[0018] Selection of the physical dimensions and Young's modulus of polymer layers in composite patterning devices of the present invention establishes the overall mechanical properties of the composite patterning device, such as the net flexural rigidity and conformability of the patterning device. In an embodiment of the present invention useful for soft lithographic contact printing and molding applications the first polymer layer is characterized by a Young's modulus selected over the range of about 1 MPa to about 10 MPa and a thickness selected over the range of about 1 micron to about 100 microns, and the second polymer layer is characterized by a Young's modulus selected over the range of about 1 GPa to about 10 GPa and a thickness selected over the range of about 10 microns to about 100 microns. Composite patterning devices of the present useful for soft lithographic contact printing applications also include embodiments wherein the ratio of the thickness of the first polymer layer and the thickness of the second polymer layer is selected from the range of about 1 to about 10, preferably equal to about 5 for some applications. In one embodiment, the first polymer is an

elastomeric layer, such as a PDMS or h-PDMS layer, the second polymer layer is a thermoplastic or thermoset layer, such as a polyimide layer, and the composite patterning device has a net flexural rigidity selected from the range of about 1×10^{-7} Nm to about 1×10^{-5} Nm.

[0019] Use of a low modulus first polymer layer, such as an elastomer layer, is beneficial in the present invention because it provides patterning devices having the capability to establish conformal contact with large areas (up to several m^2) of smooth surfaces, flat surfaces, rough surfaces, particularly surfaces having roughness amplitudes up to about 1 micron, and contoured surfaces, preferably surfaces having radii of curvature up to about 25 microns. In addition, use of a low modulus first polymer layer allows conformal contact to be established between the contact surface(s) and large areas of substrate surface using relative low pressures (about 0.1 kN m^{-2} to about 10 kN m^{-2}) applied to the external surface of the second polymer layer. For example, a low modulus first polymer layer comprising a PDMS layer having a thickness greater than or equal to about 5 microns establishes reproducible conformal contact over substrate surface areas as large as 250 cm^2 upon application of external pressures less than or equal to about 100 N m^{-2}. In addition, incorporation of a low modulus first polymer layer into patterning devices of the present invention allows conformal contact to be established in a gradual and controlled manner, thus, avoiding the formation of trapped air pockets between the contact surface of the first layer and a substrate surface. Further, incorporation of a low modulus first polymer layer provides good release characteristics of contact surfaces from substrate surfaces and the surfaces of master relief patterns used to make composite patterning devices of the present invention.

[0020] Use of a high modulus second polymer layer in patterning devices of the present invention is beneficial because it provides patterning devices having a net flexural rigidity large enough to minimize distortions of the relief pattern which may occur upon formation of conformal contact between the contact surface(s) and a substrate surface. First, incorporation of a high modulus second polymer layer into patterning devices of the present invention minimizes distortions of the relief pattern in planes parallel to a plane containing the contact surface, such as distortions characterized by the collapse of narrow relief features of patterns having high

aspect ratios. Second, incorporation of a high modulus second polymer layer minimizes distortions of the relief pattern in planes which intersect a plane containing the contact surface, such as distortions characterized by sagging of recessed regions of a relief pattern. This reduction in relief pattern distortion provided by incorporation of a high modulus second polymer layer allows patterns of small structures comprising well defined features having physical dimensions as small as 50 nanometers to be fabricated using patterning devices and methods of the present invention.

[0021] Use of a high modulus second polymer layer in patterning devices of the present invention is also beneficial because it allows for easy handling and incorporation of patterning devices of the present invention into printing, embossing and molding machines. This attribute of the present invention facilitates mounting, remounting, orienting, maintaining and cleaning of the present patterning devices. Incorporation of a high modulus second polymer layer also improves the accuracy in which patterning devices of the present invention may be brought into contact with a selected region of a substrate surface by a factor of 25 with respect to conventional single layer PDMS stamps, molds and photomasks. For example, incorporation of a 25 micron thick second polymer layer having a Young's modulus equal to or greater than 5 GPa, such as a polyimide layer, allows patterning devices of the present invention to be brought into contact with a substrate surface with a placement accuracy equal to about 1 micron over a substrate area equal to about 232 cm^2. Further, use of a flexible and resilient, high modulus second polymer layer allows patterning devices of the present invention to be operated in a range of device configurations and easily integrated into conventional printing and molding systems. For example, use of a second polymer layer having a flexural rigidity of about 7×10^{-6} Nm allows integration of pattering devices of the present invention into conventional roller and flexographic printing systems.

[0022] In an alternative embodiment, a patterning device of the present invention comprises a unitary polymer layer. The unitary polymer layer comprises a three-dimensional relief pattern having at least one contact surface disposed thereon and a base having an external surface positioned opposite to the contact surface. The contact surface is oriented orthogonal to a layer alignment axis extending through

the polymer layer, and the Young's modulus of the polymer layer varies continuously along the layer alignment axis from the contact surface to the external surface of the base. In one embodiment, the Young's modulus of the polymer layer varies continuously along the layer alignment axis from a low value at the contact surface to a high value at the mid point between the contact surface and the external surface along the layer alignment axis. In another embodiment, the Young's modulus of the polymer layer varies continuously from a high modulus value at the mid point between the contact surface and the external surface along the layer alignment axis to a low modulus value at the external surface of the base. Optionally, the polymer layer may also have a substantially symmetrical distribution of the coefficients of thermal expansion about the center of the patterning device along the layer alignment axis. Variation of the Young's modulus in the polymer layer may be achieved by any means known in the art including methods wherein the extent of cross linking in the unitary polymer layer is selectively varied to achieve control of the Young's modulus as a function of position along the layer alignment axis.

[0023] Three-dimensional relief patterns useable in the present invention may comprise a singular continuous relief feature or a plurality of continuous and/or discrete relief features. In the present invention, selection of the physical dimensions of relief features or their arrangement in a relief pattern is made on the basis of the physical dimensions and relative arrangements of the structures to be generated on a substrate surface. Relief patterns useable in composite patterning devices of the present invention may comprise relief features having physical dimensions selected over the range of about 10 nanometers to about 10,000 nanometers, preferably selected over the range of about 50 nanometers to about 1000 nanometers for some applications. Relief patterns useable in the present invention may comprise symmetrical patterns of relief features or asymmetrical patterns of relief features. Three-dimensional relief patterns may occupy a wide range of areas, and relief areas selected over the range of about 10 cm^2 to about 260 cm^2 are preferred for some micro- and nanofabrication applications.

[0024] In another embodiment, a composite patterning device of the present invention further comprises a third polymer layer having an internal surface and an

external surface. In this three layer embodiment, the first, second and third polymer layers are arranged such that a force applied to the external surface of the third polymer layer is transmitted to the first polymer layer. For example, first, second and third polymer layers may be arranged such that a force applied to the external surface of the third layer is transmitted to at least a portion of the contact surface(s) of the first polymer layer. In an embodiment, the external surface of the second polymer layer is operationally coupled to the internal surface of the third polymer layer. For example, the external surface of the second polymer layer may be in physical contact with the internal surface of the third polymer layer. Alternatively, the second polymer layer and the third polymer layer may be connected by one or more connecting layers, such as thin metal layers, polymer layers or ceramic layers, positioned between the external surface of the second polymer layer and the internal surface of the third polymer layer. Optionally, the third polymer layer may be operationally coupled to an actuator capable of providing an external force to the external side of the third polymer layer so as to bring the contact surface(s) of the patterning device into conformal contact with the substrate surface undergoing patterning. Incorporation of a third polymer layer may also provide a means of handing, positioning, orienting, mounting, cleaning and maintaining composite patterning devices of the present invention.

[0025] Incorporation of a third polymer layer having a low young's modulus into composite patterning devices of the present invention is beneficial for some soft lithography applications. First, use of a low Young's modulus third polymer layer allows the force applied to the patterning device to be applied in a gradual and controlled manner, facilitating generation of conformal without formation of trapped air bubbles. Second, integration of a low Young's modulus third polymer layer provides an effective means of uniformly distributing a force applied to the patterning device to the contact surface(s) of the first polymer layer. Uniform distribution of the force applied to the patterning device to the contact surface(s) promotes formation of conformal contact over large areas of the substrate surface and enhances the fidelity of patterns generated on a substrate surface. In addition, uniform distribution of the force applied to the patterning device to the contact surface(s) improves the overall efficiency and energy consumption of the patterning

process. An exemplary third polymer layer has a thickness which is several times thicker than the roughness and/or radius of curvature of the substrate surface.

[0026] In another aspect, the present invention provides thermally stable composite patterning devices that undergo less thermal induced pattern distortion than conventional single layer and multiple layer stamps, molds and photomasks. Some materials having a low Young's modulus are also characterized by a large coefficient of thermal expansion. For example, PDMS has a Young's modulus of 3 MPa and a coefficient of thermal expansion equal to about 260 ppm. Increases or decreases of temperature, therefore, can result in substantial distortions in relief patterns comprising these materials, particularly for patterning devices having large area relief patterns. Relief pattern distortions caused by changes in temperature may be especially problematic for applications involving fabrication of patterns of structures having features with very small dimensions, such as submicron sized structures, over large areas of substrate

[0027] In one aspect of the present invention, a plurality of layers having different mechanical properties and/or thermal expansion coefficients are combined and matched in a manner providing patterning devices exhibiting high thermal stability. In another aspect of the present invention, a plurality of layers are combined such that the net thermal expansion properties of the patterning device is matched to the thermal expansion properties of the substrate, preferably matched to with 10% for some applications. In the context of the present description, "high thermal stability" refers to patterning devices exhibiting minimal pattern distortions upon changes in temperature. Composite pattering devices of the present invention having high thermal stability exhibit reduced deformation of relief patterns and contact surfaces caused by stretching, bowing, buckling, expansion and compression induced by changes in temperature, as compared to conventional single layer and multilayer stamps, molds and photomasks. In one embodiment, a high modulus second polymer layer having a low coefficient of thermal expansion, such as a polyimide layer, is operationally coupled to the internal surface of a low modulus first polymer layer having a large coefficient of thermal expansion, such as a PDMS layer or a h-PDMS layer. In this arrangement, integration of a second polymer layer having a high modulus and low coefficient of thermal expansion constrains expansion or

contraction of the first polymer layer and, therefore, significantly decreases the extent of stretching or compression of the contact surface(s) and three-dimensional relief pattern induced by increases or decreases in temperature. In one embodiment of this aspect of the present invention, the second polymer layer has a coefficient of thermal expansion less than or equal to about 14.5 ppm and, optionally a thickness that is about five times larger than the thickness of the first layer.

[0028] In the present invention, good thermal stability may also be achieved by incorporation of a discontinuous low modulus first layer operationally coupled to a high modulus second layer, preferably a high modulus layer having a low thermal expansion coefficient. In one embodiment, the discontinuous low modulus layer is a three dimensional relief pattern comprising a plurality of discrete relief features. Discrete relief features comprising the low modulus layer are not in contact with each other but are each operationally coupled to the high modulus layer. For example, the pattern of discrete relief features may comprise a pattern of individual islands of low modulus material on the internal surface of the high modulus layer. Incorporation of a first low modulus layer comprising a plurality of discrete relief features into composite patterning devices of the present invention is beneficial because it decreases the extent of the mismatch between thermal expansion properties of the low modulus and high modulus layers. In addition, use of a discontinuous low modulus layer decreases the net amount of material having a high coefficient of thermal expansion, which decreases the net extent of expansion or contraction induced by a change in temperature. In an exemplary embodiment, the discontinuous low modulus layer comprises an elastomer, such as PDMS or h-PDMS, and the high modulus layer comprises polyimide.

[0029] In another embodiment of the present invention providing patterning devices having good thermal stability, a plurality of layers are arranged so as to provide a substantially symmetrical distribution of coefficients of thermal expansion, thicknesses or both about the center of the patterning device along a layer alignment axis extending through the patterning device, for example a layer alignment axis positioned orthogonal to the contact surface. In an alternative embodiment also exhibiting good thermal stability, a temperature compensated

patterning device of the present invention comprises a unitary polymer layer having a substantially symmetrical distribution of coefficients of thermal expansion about the center of the patterning device along a layer alignment axis extending through the patterning device, for example positioned orthogonal to the contact surface.

[0030] The symmetrical distribution of coefficients of thermal expansion, thicknesses or both in these configurations provides a means of compensating for the thermal expansion or compression of one or more layers. The result of this compensation scheme is to minimize buckling, bowing, elongation and compression of the relief pattern induced by changes in temperature. Particularly, a symmetrical distribution of coefficients of thermal expansion and layer thicknesses generates opposing forces having approximately the same magnitude but opposite directions upon a change in temperature. Accordingly, this temperature compensation scheme is used to minimize the magnitude of forces generated upon a change in temperature which act on the contact surface, relief features and three-dimensional relief pattern of the first layer.

[0031] An exemplary temperature compensated patterning device of the present invention comprises three layers having mechanical and physical properties selected to provide a substantially symmetrical distribution of thermal expansion coefficients about the center of the device. The first layer comprises a three-dimensional relief pattern having at least one contact surface disposed thereon and an internal surface positioned opposite the contact surface. The first layer also has a low Young's modulus, for example ranging from about 1 MPa to about 10 MPa. The second layer has an internal surface and an external surface, and a high Young's modulus, for example ranging from about 1 GPa to about 10 GPa. The third layer has an internal surface and an external surface. In this three layer embodiment, the first, second and third layers are arranged such that a force applied to the external surface of the third layer is transmitted to the contact surface of the first layer. The thicknesses and thermal expansion coefficients of the first and third layers may be selected to provide a substantially symmetrical distribution of the coefficients of thermal expansion about the center of the patterning device along a layer alignment axis extending through said patterning device, such as a

PCT/US05/14449
layer alignment axis positioned orthogonal to a plane encompassing at least one contact surface.

[0032] An exemplary three layer composite patterning device exhibiting high thermal stability comprises a PDMS first layer, a polyimide second layer and a PDMS third layer. In this embodiment, the thickness of first and third PDMS layers may be substantially equal, for example within 10% of each other, to provide a substantially symmetrical distribution of coefficients of thermal expansion about the center of the device along a layer alignment axis extending orthogonal to the contact surface. In this embodiment, pattern distortions across a 1 cm^2 relief pattern less than 150 nanometers for a change in temperature of 1 K are observed for three layer patterning devices of the present invention having first and third PDMS layers comprising the same material, having thicknesses equal to about 5 microns and separated by an approximately 25 micron thick polyimide layer. In an embodiment of the present invention having matched first and third layers providing a substantially symmetrical distribution of coefficients of thermal expansion, the ratio of the relief depth to the thickness of the first layer is kept small (e.g. less than or equal to 0.10) to avoid unwanted temperature induced thermal expansion or contraction corresponding to thermal coefficient mismatching in recessed regions of the relief pattern.

[0033] In another aspect, the present invention provides composite patterning devices that undergo less pattern distortion caused by polymerization and curing during fabrication than conventional single layer and multiple layer stamps, photomasks and molds. Many polymers, such as PDMS, undergo a significant decrease in their physical dimensions upon polymerization. As relief patterns used in pattering devices are typically fabricated by initiating polymerization of a prepolymer in contact with a master relief surface, such as a master relief surface generated by conventional photolithography methods, this shrinkage may significantly distort the physical dimensions of relief patterns and contact surfaces of pattering devices comprising polymeric materials, particularly elastomers.

[0034] The present invention provides multilayer stamp designs that are less susceptible to deformations caused by polymerization and curing during fabrication.

PCT/US05/14449
Composite pattering devices of the present invention having decreased susceptibility to curing induced deformations of relief patterns and contact surfaces exhibit less stretching, bowing, buckling, expansion and compression induced by polymerization reactions during fabrication, as compared to conventional single layer and multilayer stamps, molds and photomasks. In one embodiment, a plurality of polymer layers having specific mechanical and thermal expansion characteristics are combined and/or matched in a manner decreasing the net extent of pattern distortion generated upon polymerization and curing during fabrication.

[0035] A composite patterning device of the present invention having decreased sensitivity to curing induced deformations of relief patterns and contact surfaces further comprises third and fourth polymer layers, each have internal surfaces and external surfaces. In this four layer embodiment, the first, second, third and fourth polymer layers are arranged such that a force applied to the external surface of the fourth polymer layer is transmitted to the contact surface of the first polymer layer. For example, first, second, third and fourth polymer layers may be arranged such that a force applied to the external surface of the fourth layer is transmitted to at least a portion of the contact surfaces of the first polymer layer. In an embodiment, the external surface of the second polymer layer is operationally coupled to the internal surface of the third polymer layer and the external surface of the third polymer layer is operationally coupled to the internal surface of the fourth polymer layer. Improved resistance to curing and/or polymerization induced distortion may be provided by matching the thicknesses, coefficients of thermal expansion and Young's modulus of the first and third layers and by matching the thicknesses, coefficients of thermal expansion and Young's modulus of the second and fourth layers. The net result of this matched multilayer design is to decrease the extent of curing induced distortions by a factor of about 10 relative to conventional single layer or double layer stamps, molds and photomasks.

[0036] Composite patterning devices of the present invention may be fully optically transmissive or partially optically transmissive, particularly with respect to electromagnetic radiation having wavelengths in the ultraviolet and/or visible regions of the electromagnetic spectrum. Patterning devices which transmit visible light are preferred for some applications because they can be visually aligned with a

substrate surface. Patterning devices of the present invention may transmit one or more patterns of electromagnetic radiation onto the substrate surface characterized by selected two dimensional distributions of intensities, wavelengths, polarization states or any combination of these. The intensities and wavelengths of electromagnetic radiation transmitted by patterning devices of the present invention may be controlled by introduction of materials into the polymer layers having selected absorption properties, scattering properties and/or reflection properties. In an exemplary embodiment, the patterning device is a partially transparent optical element characterized by a selected two dimensional distribution of absorption coefficients, extinction coefficients, reflectivities or any combination of these parameters. An advantage of this design is that it results in a selected two dimensional distribution of the intensities and wavelengths electromagnetic radiation transmitted to the substrate upon illumination by an optical source, such as a broad band lamp, atomic lamp, blackbody source or laser.

[0037] In one embodiment, the present invention comprises an optically transmissive mold capable of transmitting electromagnetic radiation for inducing polymerization reactions in a transfer material disposed between the relief pattern of the first layer of the patterning device and the substrate surface. In another embodiment, the present invention comprises an optically transmissive photomask capable of transmitting a pattern of electromagnetic radiation on to a substrate surface in conformal contact with the contact surface of the first layer of the patterning device. In another embodiment, the present invention comprises an optically transmissive stamp capable of illuminating materials transferred to the surface of a substrate.

[0038] The present invention provides highly versatile patterning devices that may be used in a wide range of soft lithography methods, microfabrication methods and nanofabrication methods. Exemplary fabrication methods compatible with the patterning devices of the present invention include, but are not limited to, nanotransfer and/or microtransfer printing, nanotransfer and/or microtransfer molding, replica molding, nanomolding and micromolding in capillaries, near field phase shift lithography, and solvent assisted nanomolding and micromolding. In addition, patterning devices of the present invention are compatible with a wide

variety of contact surface orientations including but not limited to planar, contoured, convex and concave contact surface configurations, which allow their integration into many different printing, molding and masking systems. In some applications, the coefficient of thermal expansion and thickness of polymer layers comprising a patterning device of the present invention are selected such that the net thermal expansion properties of the patterning device matches the thermal expansion properties of the substrate undergoing patterning. Matching thermal properties of the patterning device and the substrate is beneficial because it results in improved placement accuracy and fidelity of patterns fabricated on substrate surfaces.

[0039] In another aspect, the present invention provides methods of generating one or more patterns on a substrate surface by contact printing a transfer material, including methods of microtransfer contact printing and nanotransfer contact printing. In one embodiment, a transfer material is deposited onto the contact surface of a composite patterning device of the present invention, thereby generating a layer of transfer material on the contact surface. Deposition of transfer material onto the contact surface may be achieved by any means known in the art including, but not limited to, vapor deposition, sputtering deposition, electron beam deposition, physical deposition, chemical deposition dipping and other methods which involve bringing the contact surface into contact with a reservoir of transfer material. The patterning device is contacted to the substrate surface in a manner establishing conformal contact between at least a portion of the contact surface and the substrate surface. Establishing conformal contact exposes at least a portion of the layer of transfer material to the substrate surface. To generate a pattern on the substrate surface, the patterning device is separated from the substrate surface, thus transferring at least a portion of the transfer material to the substrate surface. The present invention also includes fabrication methods wherein these steps are sequentially repeated to construct complex structures comprising patterned multilayer stacks.

[0040] In another aspect, the present invention provides methods of generating one or more patterns on a substrate surface by molding a transfer material, such as micromolding and nanomolding methods. In one embodiment, a composite patterning device of the present invention is brought into contact with a substrate

surface in a manner establishing conformal contact between at least a portion of the contact surface and the substrate surface. Conformal contact generates a mold comprising the space separating the three-dimensional relief pattern and the substrate surface. A transfer material, such as a prepolymer, is introduced into the mold. To generate a pattern on the substrate surface, the patterning device is separated from the substrate surface, thus transferring at least a portion of the transfer material onto the substrate surface. Optionally, methods of the present invention may further comprise the steps of heating the transfer material in the mold, exposing the transfer material in the mold to electromagnetic radiation or adding a polymerization activator to the transfer material in the mold to initiate chemical changes such as polymerization and/or cross linking chemical reactions.

[0041] In another aspect, the present invention provides methods of generating one or more patterns on a substrate surface by contact photolithography. In one embodiment, a composite patterning device of the present invention is brought into contact with a substrate surface comprising one or more radiation sensitive materials in a manner establishing conformal contact between at least a portion of the contact surface and the substrate surface. Electromagnetic radiation is directed through the patterning device and onto the surface of the substrate, thereby generating a pattern of electromagnetic radiation on the substrate surface having selected two dimensional distributions of intensities, wavelengths and/or polarization states. Interactions between electromagnetic radiation and radiation sensitive materials of the substrate generate chemically and/or physically modified regions of the substrate surface, thereby generating one or more patterns on the substrate surface. Optional, methods of the present invention may further comprise the steps of removing at least a portion of the chemically modified regions of the substrate surface or removing at least a portion of the substrate surface which is not chemically modified. Material removal in this aspect of the present invention may be achieved by any means known in the art of photolithography, including but not limited to, chemical etching and exposure to chemical agents, such as solvents.

[0042] The methods, devices and device components of the present invention are capable of generating patterns on the surfaces of a wide variety of substrates including but not limited to, plastics, glasses, carbonaceous surfaces, metals,

textiles, ceramics or composites of these materials. The methods, devices and device components of the present invention are also capable of generating patterns on substrate surfaces having a wide range of surface morphologies, such as rough surfaces, smooth surfaces, contoured surfaces and flat surfaces. Important in fabricating high resolution patterns characterized by good placement accuracy and high fidelity is the use of conformable contact surfaces that support strong associations between the molecules comprising a substrate surface and molecules of the contact surface. For example, PDMS contact surfaces undergo strong Vander Waals interactions with many substrate surfaces including surfaces comprised of plastics, polyimide layers, glasses, metals, metalloids, silicon and silicon oxides, carbonaceous materials, ceramics, textiles and composites of these materials.

[0043] The methods of the present invention are capable of fabricating microscale and nanoscale structures having a wide variety of physical dimensions and relative arrangements. Symmetrical and asymmetrical three-dimensional structures may be fabricated by the present methods. The present methods, devices and device components may be used to generate patterns comprising one or more structures having features with dimensions ranging from about 10 nanometers to about 100 microns or more preferably for some applications ranging from about 10 nanometer to about 10 microns. Structures generated by the present methods, devices and device components may have selectable lengths in two or three physical dimensions, and may comprise patterned multilayer stacks. The present methods may also be used to generate structures comprising self assembled monolayers and structures. The methods, devices and device components of the present invention are capable of generating patterns comprising a wide range of materials including, but not limited to, metals, organic compounds, inorganic compounds, colloidal materials, suspensions, biological molecules, cells, polymers, microstructures, nanostructures and salt solutions.

[0044] In another aspect, the present invention comprises methods of making composite patterning devices. An exemplary method of making a composite pattering device comprises the steps of: (1) providing a master relief pattern having a selected three-dimensional relief pattern; (2) contacting the master relief pattern

PCT/US05/14449

with a prepolymer of a low modulus polymer; (3) contacting the prepolymer material with an high modulus polymer layer; (4) polymerizing the prepolymer, thereby generating a low modulus polymer layer in contact with the high modulus polymer layer and in contact with the master relief pattern; the low modulus layer having a three-dimensional relief pattern and (5) separating the low modulus layer from the master relief pattern, thereby making the composite pattering device. Master relief patterns useable in the present methods include relief patterns prepared using photolithography methods. In the present invention, polymerization may be initiated using any method known in the art including, but not limited to, thermal induced polymerization methods and electromagnetic radiation induced polymerization methods.

BRIEF DESCRIPTION OF THE DRAWINGS

[0045] Fig. 1A is a schematic showing a cross sectional view of a composite patterning device of the present invention comprising two polymer layers. Fig. 1B is a schematic showing a cross sectional view of another composite patterning device of the present invention comprising two polymer layers and exhibiting high thermal stability. Fig. 1C is a schematic showing a cross sectional view of a composite patterning device of the present invention comprising three polymer layers and exhibiting high thermal stability. Fig. 1D is a schematic showing a cross sectional view of a composite patterning device of the present invention comprising four polymer layers and exhibiting good resistance to pattern deformations caused by polymerization and/or curing during fabrication

[0046] Fig. 2A is a schematic showing an exemplary master relief pattern and an exemplary patterning device fabricated from this master relief pattern. Fig. 2B shows a scanning electron microscopy image of the relief structure of an exemplary patterning device comprising a composite stamp made using the methods of the present invention.

[0047] Fig. 3A is a schematic diagram illustrating a method for making a composite patterning device of the present invention. Fig. 3B is a schematic diagram illustrating an alternative method for making a composite patterning device of the present invention

[0048] Fig. 4A shows a schematic illustration of an exemplary patterning device of the present invention comprising a composite stamp. Fig. 4B shows a cross section scanning electron microscopy image of an exemplary composite stamp of the present invention

[0049] Figures 5A and 5B shows distortions that correspond to measurements of positions of features on an exemplary composite stamp compared to those on its master.

[0050] Figs. 6A and 6B show top view optical micrographs that illustrate the reduced tendency for sagging of recessed areas in a composite stamp of the present invention. Figure 6A corresponds to a conventional single layer PDMS stamp and Figure 6B corresponds to a composite stamp of the present invention.

[0051] Fig. 7 shows the extent of shrinkage observed after curing a four layer composite stamp of the present invention comprising a first PDMS layer, a second polyimide layer, a third PDMS layer and a fourth polyimide layer.

[0052] Fig. 8 is a schematic illustration of an exemplary nanotransfer printing processes using a composite stamp of the present invention.

[0053] Figs 9A-D show scanning electron micrographs of patterns of Ti/Au (2 nm / 20 nm) generated using composite stamps of the present invention.

[0054] Fig. 10 shows the extent of distortion during thermal induced polymerization calculated for a four layer composite patterning device of the present invention.

[0055] Fig. 11A shows the extent of distortion during thermal induced polymerization calculated for a two layer composite patterning device. Fig. 11B is a plot of the radius of curvature after polymerization as a function of the thickness of the PDMS layer for the two layer pattering device. Fig. 11C is a plot of the radius of curvature after polymerization as a function of the curing temperature for the two layer pattering device.

PCT/US05/14449

[0056] Fig.12A is a schematic diagram of a composite four layer patterning device comprising two h-PDMS layers and two polyimide (Kapton ®) layers. Figure 12B shows a plot of the predicted vertical displacement of a composite four layer patterning device in units of microns as a function of position along a recessed region about 90 microns in length.

[0057] Figs. 13A-C shows the results of a computational study of horizontal distortion due to thermal/chemical shrinkage during polymerization for a two layer composite stamp of the present invention. Figure 13A is a schematic illustrating a two layer composite stamp comprising a PDMS layer of variable thickness operationally coupled to a 25 micron Kapton layer. Figure 13B is a plot of the predicted horizontal distortion as a function of the thickness of the PDMS first layer. Figure 13C is a plot of the predicted horizontal distortion as a function of the distance along the external surface of the PDMS first layer.

[0058] Figures 14A and14B provide schematic diagrams illustrating a fiber reinforced composite stamp of the present invention. Figure 14A provides a cross sectional view and Figure 14B provides a perspective view. Figure 14C provides a schematic diagram illustrating first, second, third and fourth selected orientations corresponding to second, third, fourth and fifth layers, respectively, of fiber reinforced composite stamp.

[0059] Figure 15 provides an optical image of a composite polymer layer bonded to a PDMS layer.

[0060] Figure 16 provides a schematic diagram of a composite soft photo mask of the present invention.

[0061] Figure 17A shows an optical image of a composite soft conformal photomask of the present invention and Figure 17B shows an optical image of exposed and developed photo-resist patterns on a silicon substrate.

PCT/US05/14449

[0062] Figure 18 provides a process flow diagram illustrating a method of making a composite soft conformal photomask of the present invention.

[0063] Figures 19A and 19B provide schematic diagrams showing alignment systems using a patterning agent for aligning a photomask and substrate.

[0064] Figure 20 provides a schematic diagram illustrating an exemplary patterning method of the present invention using a patterning agent that comprises an optical medium (or ink) of conformable photomask.

DETAILED DESCRIPTION OF THE INVENTION

[0065] Referring to the drawings, like numerals indicate like elements and the same number appearing in more than one drawing refers to the same element. In addition, hereinafter, the following definitions apply:

[0066] "Coefficient of thermal expansion" refers to a parameter which characterizes the change in size that a material undergoes upon experiencing a change in temperature. Linear thermal expansion coefficient is a parameter which characterizes the change in length a material undergoes upon experiencing a change in temperature and may be expressed by the equation:

$$\Delta L = \alpha L_O \Delta T \qquad \text{(I)}$$

wherein ΔL is the change in length, α is the linear coefficient of thermal expansion, L_O is the initial length and ΔT is the change in temperature. The present invention provides composite, multilayer patterning devices wherein thermal properties and physical dimensions of discrete layers are selected to provide a substantially symmetrical distribution of coefficients of thermal expansion about the center of the device along a layer alignment axis extending through the device.

[0067] "Placement accuracy" refers to the ability of a pattern transfer method or device to generate a pattern in a selected region of a substrate. "Good placement" accuracy refers to methods and devices capable of generating patterning in a select region of a substrate with spatial deviations from the absolutely correct orientation

less than or equal to 5 microns, particularly for generating patterns on plastic substrates.

[0068] "Fidelity" refers to a measure of the similarity of a pattern transferred to a substrate surface and a relief pattern on a patterning device. Good fidelity refers to similarities between a pattern transferred to a substrate surface and a relief pattern on a patterning device characterized by deviations less than 100 nanometers.

[0069] "Young's modulus" is a mechanical property of a material, device or layer which refers to the ratio of stress to strain for a given substance. Young's modulus may be provided by the expression;

$$E = \frac{(\text{stress})}{(\text{strain})} = \left(\frac{L_0}{\Delta L} \times \frac{F}{A} \right); \qquad \text{(II)}$$

wherein E is Young's modulus, L_0 is the equilibrium length, ΔL is the length change under the applied stress, F is the force applied and A is the area over which the force is applied. Young's modulus may also be expressed in terms of Lame constants via the equation:

$$E = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu}; \qquad \text{(III)}$$

wherein λ and μ are Lame constants. Young's modulus may be expressed in units of force per unit area, such as Pascal (Pa = N m^{-2}).

[0070] High Young's modulus (or "high modulus") and low Young's modulus (or "low modulus") are relative descriptors of the magnitude of Young's modulus in a given material, layer or device. In the present invention, a High Young's modulus is larger than a low Young's modulus, preferably about 10 times larger for some applications, more preferably about 100 times larger for other applications and even more preferably about 1000 times larger for yet other applications. In one

embodiment, a material having a high Young's modulus has a Young's modulus selected over the range of about 1 GPa to about 10 GPa and a material having a low Young's modulus has a Young's modulus selected over the range of about 1 MPa to about 10 MPa.

[0071] "Conformal contact" refers to contact established between surfaces and/or coated surfaces, which may be useful for fabricating structures on a substrate surface. In one aspect, conformal contact involves a macroscopic adaptation of one or more contact surfaces of a composite patterning device to the overall shape of a substrate surface. In another aspect, conformal contact involves a microscopic adaptation of one or more contact surfaces of a composite patterning device to a substrate surface leading to an intimate contact with out voids. The term conformal contact is intended to be consistent with use of this term in the art of soft lithography. Conformal contact may be established between one or more bare contact surfaces of a composite patterning device and a substrate surface. Alternatively, conformal contact may be established between one or more coated contact surfaces, for example contact surfaces having a transfer material and/or patterning agent deposited thereon, of a composite patterning device and a substrate surface. Alternatively, conformal contact may be established between one or more bare or coated contact surfaces of a composite patterning device and a substrate surface coated with a material such as a transfer material, patterning agent, solid photoresist layer, prepolymer layer, liquid, thin film or fluid. In some embodiments of the present invention, pattering devices of the present invention are capable of establishing conformal contact with flat surfaces. In some embodiments of the present invention, pattering devices of the present invention are capable of establishing conformal contact with contoured surfaces. In some embodiments of the present invention, pattering devices of the present invention are capable of establishing conformal contact with rough surfaces. In some embodiments of the present invention, pattering devices of the present invention are capable of establishing conformal contact with smooth surfaces.

[0072] "Flexural rigidity" is a mechanical property of a material, device or layer which refers to the ability of a material, device or layer to be deformed. Flexural rigidity may be provided by the expression:

$$D = \frac{Eh^3}{12\left(1-\nu^2\right)} \qquad \text{(IV)}$$

wherein D is flexural rigidity, E is Young's modulus, h is thickness and ν is the Poisson ratio. Flexural rigidity may be expressed in units of force multiplied by unit length, such as Nm.

[0073] "Polymer" refers to a molecule comprising a plurality of repeating chemical groups, typically referred to as monomers. Polymers are often characterized by high molecular masses. Polymers useable in the present invention may be organic polymers or inorganic polymers and may be in amorphous, semi-amorphous, crystalline or partially crystalline states. Polymers may comprise monomers having the same chemical composition or may comprise a plurality of monomers having different chemical compositions, such as a copolymer. Cross linked polymers having linked monomer chains are particularly useful for some applications of the present invention. Polymers useable in the methods, devices and device components of the present invention include, but are not limited to, plastics, elastomers, thermoplastic elastomers, elastoplastics, thermostats, thermoplastics and acrylates. Exemplary polymers include, but are not limited to, acetal polymers, biodegradable polymers, cellulosic polymers, fluoropolymers, nylons, polyacrylonitrile polymers, polyamide-imide polymers, polyimides, polyarylates, polybenzimidazole, polybutylene, polycarbonate, polyesters, polyetherimide, polyethylene, polyethylene copolymers and modified polyethylenes, polyketones, poly(methyl methacrylate, polymethylpentene, polyphenylene oxides and polyphenylene sulfides, polyphthalamide, polypropylene, polyurethanes, styrenic resins, sulphone based resins, vinyl-based resins or any combinations of these.

[0074] "Elastomer" refers to a polymeric material which can be stretched or deformed and return to its original shape without substantial permanent deformation. Elastomers commonly undergo substantially elastic deformations. Exemplary elastomers useful in the present invention may comprise, polymers,

copolymers, composite materials or mixtures of polymers and copolymers. Elastomeric layer refers to a layer comprising at least one elastomer. Elastomeric layers may also include dopants and other non-elastomeric materials. Elastomers useful in the present invention may include, but are not limited to, silicon containing polymers such as polysiloxanes including poly(dimethyl siloxane) (i.e PDMS and h-PDMS), poly(methyl siloxane), partially alkylated poly(methyl siloxane), poly(alkyl methyl siloxane) and poly(phenyl methyl siloxane), silicon modified el;astomers, thermoplastic elastomers, styrenic materials, olefenic materials, polyolefin, polyurethane thermoplastic elastomers, polyamides, synthetic rubbers, polyisobutylene, poly(styrene-butadiene-styrene), polyurethanes, polychloroprene and silicones.

[0075] “Polymer layer” refers to a layer that comprises one or more polymers. Polymer layers useful in the present invention may comprise a substantially pure polymer layer or a layer comprising a mixture of a plurality of different polymers. Polymer layers useful in the present invention also include multiphase polymeric layers and/or composite polymeric layers comprising a combination of one or more polymer and one or more additional material, such as a dopant or structural additive. Incorporation of such additional materials into polymer layers of the present invention is useful for selecting and adjusting the mechanical properties of polymer layers, such as the Young’s modulus and the flexural rigidity. The distribution of additional materials in composite polymer layers may be isotropic, partially isotropic or non isotropic. Useful in composite polymeric layers of the present invention comprise one or more polymer (i) in combination with fibers, such as glass fibers or polymeric fibers, (ii) in combination with particles, such as silicon particles and/or nanosized particles, and/or (iii) in combination with other structural enhancers. In an embodiment of the present invention, a polymer layer having a high Young’s modulus comprises a polymer having a Young’s modulus selected over the range of about 1 GPa to about 10 GPa. Exemplary high Young’s modulus polymer layers may comprise polyimide, polyester, polyetheretherketone, polyethersulphone, polyetherimide, polyethyleneapthalate, polyketones, poly(phenylene sulfide) any combinations of these materials or other polymeric materials having similar mechanical properties. In an embodiment of the present invention, a polymer layer having a low Young’s modulus comprises a polymer

having a Young's modulus selected over the range of about 1 MPa to about 10 MPa. Exemplary low Young's modulus polymer layers may comprise elastomers such as, PDMS, h-PDMS polybutadiene, polyisobutylene, poly(styrene-butadiene-styrene), polyurethanes, polychloroprene and silicones.

[0076] "Composite" refers to a material, layer, or device that comprises more than one component, such as more than one material and/or phase. The present invention provides composite patterning devices comprising a plurality of polymer layers having different chemical compositions and mechanical properties. Composite polymer layers of the present invention include layers comprising a combination of one or more polymer and a fiber, such as a glass or elastomeric fiber, particulate, such as nanoparticles or microparticles or any combinations of these.

[0077] "Elastomer" refers to a polymeric material which can be stretched or deformed and return to its original shape without substantial permanent deformation. Elastomers commonly undergo substantially elastic deformations. Exemplary elastomers useful in the present invention may comprise, polymers, copolymers, composite materials or mixtures of polymers and copolymers. Elastomeric layer refers to a layer comprising at least one elastomer. Elastomeric layers may also include dopants and other non-elastomeric materials. Elastomers useful in the present invention may include, but are not limited to, PDMS, h-PDMS, polybutadiene, polyisobutylene, poly(styrene-butadiene-styrene), polyurethanes, polychloroprene and silicones.

[0078] The term "electromagnetic radiation" refers to waves of electric and magnetic fields. Electromagnetic radiation useful for the methods of the present invention includes, but is not limited to, gamma rays, X-rays, ultraviolet light, visible light, infrared light, microwaves, radio waves or any combination of these.

[0079] The terms "intensity" and "intensities" refers to the square of the amplitude of an electromagnetic wave or plurality of electromagnetic waves. The term amplitude in this context refers to the magnitude of an oscillation of an electromagnetic wave. Alternatively, the terms "intensity" and "intensities" may refer

to the time average energy flux of a beam of electromagnetic radiation or plurality of electromagnetic radiation, for example the number of photons per square centimeter per unit time of a beam of electromagnetic radiation or plurality of beams of electromagnetic radiation.

[0080] "Actuator" refers to a device, device component or element capable of providing a force and/or moving and/or controlling something. Exemplary actuators of the present invention are capable of generating a force, such as a force that is used to bring a patterning device into contact, such as conformal contact, with a substrate surface.

[0081] "Layer" refers to an element of a composite patterning device of the present invention. Exemplary layers have physical dimensions and mechanical properties which provide composite patterning devices capable of fabricating patterns on substrate surfaces having excellent fidelity and good placement accuracy. Layers of the present invention may be a continuous or unitary body or may be a collection of discontinuous bodies, such as a collection of relief features. Layers of the present invention may have a homogenous composition or an inhomogeneous composition. An embodiment of the present invention provides a composite patterning device comprising a plurality of layers, such as polymer layers. Layers in the present invention may be characterized in terms of their thickness along a layer alignment axis which extends through a patterning device, such as a layer alignment axis which is positioned orthogonal to a plane containing one or more contact surfaces.

[0082] "Thermally stable" refers to the characteristic of a device or device component to withstand a change in temperature without a loss of characteristic properties, such as the physical dimensions and spatial distribution of relief features of a relief pattern.

[0083] "Substantially symmetrical distribution of the coefficients of thermal expansion about the center of a patterning device" refers to a device configuration wherein the mechanical and thermal properties of one or more layers comprising a patterning device are selected such that there is a substantially symmetrical

distribution about the center of the patterning device along a layer alignment axis, for example a layer alignment axis which is oriented perpendicular to a plane containing one or more contact surfaces. In one embodiment, the coefficients of thermal expansion are characterized by a symmetrical distribution about the center of the patterning device with deviations from an absolutely symmetric distribution less than about 10%. In another embodiment, the coefficients of thermal expansion are characterized by a symmetrical distribution about the center of the patterning device with deviations from an absolutely symmetric distribution less than about 5%.

[0084] "Operationally coupled" refers to a configuration of layers and/or device components of composite patterning devices of the present invention. Operationally coupled layers or device components, such as first, second, third and/or fourth polymer layers, refers to an arrangement wherein a force applied to a layer or device component is transmitted to another layer or device component. Operationally coupled layers or device components may be in contact, such as layers having internal and/or external surfaces in physical contact. Alternatively, operationally coupled layers or device components may be connected by one or more connecting layers, such as thin metal layers, positioned between the internal and/or external surfaces of two layers or device components.

[0085] In the following description, numerous specific details of the devices, device components and methods of the present invention are set forth in order to provide a thorough explanation of the precise nature of the invention. It will be apparent, however, to those of skill in the art that the invention can be practiced without these specific details.

[0086] This invention provides methods, devices and device components for fabricating patterns on substrate surfaces, such as patterns comprising microsized structures and/or nanosized structures. The present invention provides composite patterning devices, such as stamps, molds and photomasks, exhibit enhanced thermal stability and resistance to curing induced pattern distortions. The methods, devices and device components of the present invention are capable of generating high resolution patterns exhibiting good fidelity and excellent placement accuracy.

[0087] Figure 1A is a schematic showing a cross sectional view of a composite patterning device of the present invention comprising two polymer layers. The illustrated composite patterning device **100** comprises a first polymer layer **110** having a low Young's modulus and a second polymer layer **120** having a high Young's modulus. First polymer layer **110** comprises a three-dimensional relief pattern **125** having a plurality of relief features **133** separated by a plurality of recessed regions **134**. First polymer layer **110** also has a plurality of contact surfaces **130** positioned opposite to an internal surface **135**. The present invention includes embodiments wherein contact surfaces **130** occupy a common plane and embodiments wherein contact surfaces **130** occupy more than one plane. Second polymer layer **120** has an internal surface **140** and an external surface **150**. In the embodiment shown in Figure 1A, the internal surface **135** of first polymer layer **110** is positioned in contact with internal surface **140** of second polymer layer **120**. Optionally, second polymer layer **120** is operationally connected to actuator **155** which is capable of directing a force (schematically shown as arrows **156**) onto external surface **150**.

[0088] First polymer layer **110** and second polymer layer **120** may be coupled in any manner allowing a force exerted on external surface **150** to be transmitted effectively to contact surfaces **130**. In exemplary embodiments, first polymer layer **110** and second polymer layer **120** are coupled via covalent bonding between the polymers comprising each layer. Alternatively, first polymer layer **110** and second polymer layer **120** may be coupled by attractive intermolecular forces between each layer, such as Van der Waals forces, dipole-dipole forces, hydrogen bonding and London forces. Alternatively, first polymer layer **110** and second polymer layer **120** may be coupled by an external layer alignment system, such as clamping, fastening and/or bolting systems. Alternatively, first polymer layer **110** and second polymer layer **120** may be coupled using one or more connecting layers (not shown in Fig. 1A), such as thin metal layers, positioned between internal surface **135** and internal surface **140**. Coupling of first polymer layer **110** and second polymer layer **120** via strong covalent bonding and/or attractive intermolecular forces is preferred for some applications because is provides good mechanical rigidity to relief features **133** and

recessed areas **134,** and also provides an effective means of evenly distributing forces applied to external surface **150** to contact surfaces **130**.

[0089] In the exemplary embodiment shown in Figure 1A, the composition, Young's modului and/or thicknesses along a layer alignment axis **160** positioned orthogonal to a plane including contact surfaces **130** of first polymer layer **110** are selected to provide mechanical properties of patterning device **100** that allow fabrication of high resolution patterns of microsized and/or nanosized structures which exhibit reduced pattern distortions. In addition, the Young's modului and/or thicknesses of first polymer layer **110** and second polymer layer **120** may also be selected to provide easy integration of the patterning device **100** into commercial printing and molding systems. In an exemplary embodiment, first polymer layer **110** comprises a PDMS layer having a thickness along the layer alignment axis **160** selected from the range of about 5 microns to about 10 microns. The thickness of first polymer layer **110** may alternatively be defined in terms of the shortest distance between contact surfaces **130** and internal surface **140** of second polymer layer **120**. In an exemplary embodiment, second polymer layer **120** comprises a polyimide layer having a thickness along the layer alignment axis equal to about 25 microns. The thickness of second polymer layer **120** may alternatively be defined in terms of the shortest distance between the internal surface **140** and external surface **150** of second polymer layer **120**.

[0090] To fabricate patterns comprising one or more structures, the composite patterning device **100** and surface **185** of substrate **180** are brought into contact with each other, preferably contact establishing conformal contact between at least a portion of contact surfaces **130** and substrate surface **185**. Conformal contact between these surfaces may be achieved by application of an external force (schematically represented by arrows **156**) onto external surface **150** in a manner moving patterning device **100** into contact with substrate **180**. Alternatively, an external force (schematically represented by arrows **190**) may be applied to substrate **180** in a manner moving substrate **180** into contact with the patterning device **100**. The present invention also includes embodiments wherein conformal contact is established by a combination of these forces (**156** and **190**) and motions of substrate **180** and patterning device **100**.

[0091] Figure 1B is a schematic showing a cross sectional view of another composite patterning device of the present invention exhibiting high thermal stability comprising two polymer layers. As shown in Fig. 1B, the composite patterning device **200** comprises a discontinuous first polymer layer **210** having a low Young's modulus operationally connected to second polymer layer **120** having a high Young's modulus. In this embodiment, discontinuous first polymer layer **210** comprises a three dimensional relief pattern **225** comprising a plurality of discrete relief features **233** separated by a plurality of recessed regions **234**. As shown in Figure 1B, discrete relief features **233** do not contact each other but are each operationally coupled to the second polymer layer **120**. Incorporation of a first polymer layer comprising a plurality of discrete relief features into composite patterning devices of the present invention is beneficial because it decreases the extent of the mismatch between thermal expansion properties of the first and second polymer layers **210** and **120**, and also decreases the net amount of material in the first polymer layer **210**, which may comprise a material having a high coefficient of thermal expansion, such as PDMS

[0092] Figure 1C is a schematic showing a cross sectional view of another composite patterning device of the present invention exhibiting high thermal stability comprising three polymer layers. The illustrated composite patterning device **300** further comprises third polymer layer **310** having an internal surface **315** and an external surface **320**. In the embodiment illustrated in Figure 1C, the internal surface **315** of third polymer layer **310** is in contact with the external surface **150** of second polymer layer **120**. Optionally, third polymer layer **310** is operationally coupled to actuator **155** which is capable of directing a force (schematically shown as arrows **156**) onto external surface **320**.

[0093] In the embodiment shown in Figure 1C, the thickness **330** of third polymer layer **310** along layer alignment axis **160** is approximately equal to the thickness **340** of first polymer layer **110** along layer alignment axis **160**, preferably within 10% for some applications. In this embodiment, selection of third polymer layer **310** and first polymer layer **110** having the same or similar (e.g. within 10%) coefficients of thermal expansion, such as both layers comprising PDMS layers, provides for high

thermal stability and resistance to pattern distortions induced by changes in temperature. Particularly, this arrangement provides a substantially symmetrical distribution of the coefficients of thermal expansion about the center (indicated by center line axis **350**) of patterning device **300** along layer alignment axis **160**. A symmetrical distribution of the coefficients of thermal expansion provides for generation of opposing forces upon a change in temperature which minimizes the extent of stretching, bowing, buckling, expansion and compression of relief pattern **125**, relief features **133** and contact surfaces **130**.

[0094] Figure 1D is a schematic showing a cross sectional view of a four layer composite patterning device of the present invention exhibiting good resistance to pattern deformations caused by polymerization and/or curing during fabrication. The illustrated composite patterning device **400** further comprises fourth polymer layer **410** having an internal surface **415** and an external surface **420**. In the embodiment, illustrated in Figure 1D, the internal surface **415** of fourth polymer layer **410** is in contact with the external surface **320** of third polymer layer **310**. Optionally, fourth polymer layer **410** is operationally connected to actuator **155** which is capable of directing a force (schematically shown as arrows **156**) onto external surface **420**.

[0095] In the embodiment shown in Figure 1D, the thickness **330** of third polymer layer **310** along layer alignment axis **160** is approximately equal to the thickness **340** of first polymer layer **110** along layer alignment axis **160**, preferably within 10% for some applications, and the thickness **430** of fourth polymer layer **410** along layer alignment axis **160** is approximately equal to the thickness **440** of second polymer layer **120** along layer alignment axis **160**, preferably within 10% for some applications. In this embodiment, selection of third polymer layer **310** and first polymer layer **110** having the same coefficients of thermal expansion and Young's modulus, such as both layers comprising PDMS layers, and selection of fourth polymer layer **410** and second polymer layer **120** having the same coefficients of thermal expansion and Young's modulus, such as both layers comprising polyimide layers, provides for good resistance to pattern distortions caused by polymerization and/or curing during fabrication. Particularly, this arrangement minimizes the extent

PCT/US05/14449
of stretching, bowing, buckling, expansion and compression of relief pattern **125** and contact surfaces **130** during polymerization and/or curing.

[0096] Surfaces of polymer layers including first, second third and fourth layers in the present invention may possess specific relief patterns, such as alignment channels and/or grooves, useful for providing proper alignment between layers. Alternatively, surfaces of polymer layers in the present invention may possess specific relief patterns, such as alignment channels and/or grooves, useful for providing proper alignment between a composite patterning device and an actuator such as a printing device, molding device or contact photolithography apparatus having complimentary (i.e. mating) channels and/or grooves. Alternatively, surfaces of polymer layers in the present invention may possess specific relief patterns, such as alignment channels and/or grooves, useful for providing proper alignment between a composite patterning device and substrate surface having complimentary (i.e. mating) channels and/or grooves. As will be understood by a person of ordinary skill in the art, use of such "lock and key" alignment mechanisms, channels, grooves and systems are well known in the art of microfabrication, and may easily be integrated into the patterning devices of the present invention.

[0097] Selection of the composition, physical dimensions and mechanical properties of polymer layers in composite patterning devices of the present invention depends largely on the material transfer method to be employed (e.g. printing, molding etc.) and the physical dimensions of the structures/patterns to be fabricated. In this sense, the composite patterning device specifications of the present invention may be regarded as selectably adjustable for a particular functional task or pattern/structure dimensions to be accomplished. For example, a two layer patterning device of the present invention useful for printing nanosized structures via soft lithographic methods may comprise an elastomeric first polymer layer having a thickness selected from the range of about 1 micron to about 5 microns, and a second polymer layer comprising a polyimide layer having a thickness less than or equal to about 25 microns. In contrast, a two layer patterning device of the present invention useful for micro-molding structures having dimensions ranging from about 10 microns to about 50 microns may comprise an elastomeric first polymer layer having a thickness selected from the range of about

PCT/US05/14449
20 microns to about 60 microns, and a second polymer layer comprising a polyimide layer having a thickness selected over the range of about 25 microns to about 100 microns.

[0098] Composite patterning devices of the present invention, such as stamps, molds and photomasks, may be made by any means known in the art of material science, soft lithography and photolithography. An exemplary patterning device of the present invention is prepared by fabricating a first polymer layer comprising an elastomer by casting and curing polydimethylsiloxane (PDMS) prepolymer (Dow Corning Sylgard 184) against a master relief pattern consisting of patterned features of photoresist (Shipley 1805) prepared by conventional photolithographic means. Master relief patterns useful in the present invention may be fabricated using conventional contact mode photolithography for features larger than about 2 microns or using electron beam lithography for features smaller than about 2 microns. In an exemplary method, PDMS (Sylgard 184 from Dow Corning) or h-PDMS (VDT-731, Gelest Corp) are mixed and degassed, poured over the masters and cured in an oven at about 80 degrees Celsius. Alternatively, curing of 184 PDMS may be performed at room temperature using extra amounts of curing agent. First polymer layers comprising PDMS or h-PDMS are preferably cured in the presence of the second high modulus layer, such as a polyimide layer, to reduce shrinkage induced by curing and/or polymerization. In one embodiment, the internal surface of the polyimide layer is roughened prior to being brought into contact with the PDMS prepolymer to enhance the strength of the binding of the PDMS first layer to the polyimide second layer upon curing of the PDMS prepolymer. Surface roughening of the polyimide layer may be achieved by any means known in the art including exposing the internal surface of the polyimide layer to a plasma.

[0099] Fabrication and curing of the additional layers in composite patterning devices, for example high modulus second polymer layers, is preferably done simultaneously with preparation of the elastomeric first layer to minimize the extent of curing and/or polymerization induced shrinkage of the relief pattern and contact surfaces of the elastomeric first layer. Alternatively, a high modulus second

polymer layer, for example polyimide layer, may be attached to the first polymer layer using an adhesive or connecting layer, such as a thin metal layer.

[00100] An exemplary master relief pattern was fabricated using a positive photoresist (S1818, Shipley,) and lift off resist (LOR1A; micron Chem.). In this exemplary method, test grade approximately 450 micron thick silicon wafers (Montco Silicon Technologies) were cleaned with acetone, iso-propanol and deionized water and then dried on a hotplate at 150 degrees Celsius for 10 minutes. LOR 1A resin was spin-coated at 3000 rpm for 30 seconds and then pre-baked on a hot plate at 130 degrees C for five minutes. Next, the S1818 resin was spin coated at 3000 rpm for 30 seconds and backed on a hot plate for 110 degrees Celsius for five minutes. The resulting bilayer (approximately 1.7 microns thick) was exposed (□ = 365 nm, 16.5 mW/cm^2) for 7 seconds with an optical contact aligner (Suss Microtech MJB3) using a chromium ion glass mask, and then developed (MF-319; Shipley) for 75 seconds. The development removed all the S1818 resist that was photoexposed. It also removed, in a roughly isotropic manner, the LOR 1A in both the exposed and unexposed regions. The result of this process is a pattern of S1818 on LOR 1A with regions of bare substrate in the exposed areas and slight undercuts at the edges of the patterns. Composite patterning devices comprising stamps were prepared from this master relief pattern using standard soft lithographic procedures of casting and curing PDMS against the master relief pattern. Figure 2A is a schematic showing an exemplary master relief pattern **461** and an exemplary patterning device **463** fabricated from this master relief pattern. Figure 2B shows a scanning electron microscopy image of the relief structure of an exemplary patterning device comprising a composite stamp made using the methods of the present invention.

[00101] Figure 3A is a schematic diagram illustrating a method for making a composite patterning device of the present invention. As shown in processing step A of Figure 3A, the patterning device may be prepared by spin coating a prepolymer of PDMS on a master relief pattern comprising resin relief features on silicon. Optionally, the master relief pattern may be treated with a self assembled monolayer of material to minimize adhesion of the PDMS first layer to the master. As shown in processing step B of Figure 3A, the PDMS first layer may be fabricated

by curing for a few hours using a hot plate and a curing temperature between about 60 and about 80 degrees Celsius. After curing, a thin film of titanium, gold or a combination of both may be deposed on the internal surface of the PDMS first layer via electron beam evaporation methods, as shown in processing step C of Figure 3A. A thin film of titanium, gold or mixture of both may also be deposed on the internal surface of the high modulus second polymer layer (see step C of Figure 3A). First and second layers are operationally coupled via cold welding the coated internal surfaces of the first and second layers, and the composite patterning device may be separated from the master relief pattern, as shown in processing step D and E of Figure 3A, respectively.

[00102] Figure 3B shows an alternative method of fabricating a composite multilayer patterning device of the present invention. As shown in processing step A of Figure 3B, the internal surface of a high modulus second layer is coated with titanium, silicon oxide or a combination of both. The coated internal side of the high modulus second layer is brought into contact with a master relief spin coated with a PDMS prepolymer and pressure is applied to the external surface of the high modulus second layer, as shown in processing step B of Figure 3B. This configuration allows the thickness of the layer of PDMS prepolymer to be selectably adjusted by spinning the master relief pattern and/or applying pressure to the external surface of the high modulus second layer with a flat or rocker based press. Upon achieving a desired thickness, the PDMS prepolymer is cured for a few hours in an oven using curing temperature ranging from about 60 to 80 degrees Celsius, thereby forming the PDMS first layer, as shown in processing step C of Figure 3B. Finally, the composite patterning device is separated from the master relief pattern. Optionally, this method includes the step of treating the master relief pattern with a self assembled monolayer of material to minimize adhesion of the PDMS first layer to the master.

[00103] The terms and expressions which have been employed herein are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should

be understood that although the present invention has been specifically disclosed by preferred embodiments, exemplary embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims. The specific embodiments provided herein are examples of useful embodiments of the present invention and it will be apparent to one skilled in the art that the present invention may be carried out using a large number of variations of the devices, device components, methods steps set forth in the present description. Methods and devices useful for the present methods can include a large number of optional device elements and components including, additional polymer layers, glass layers, ceramic layers, metal layers, microfluidic channels and elements, actuators such as rolled printers and flexographic printers, handle elements, fiber optic elements, birefringent elements such as quarter and half wave plates, optical filters such as FP etalons, high pass cutoff filters and low pass cutoff filters, optical amplifiers, collimation elements, collimating lens, reflectors, diffraction gratings, focusing elements such as focusing lens and reflectors, reflectors, polarizers, fiber optic couplers and transmitters, temperature controllers, temperature sensors, broad band optical sources and narrow band optical sources.

[00104] All references cited in this application are hereby incorporated in their entireties by reference herein to the extent that they are not inconsistent with the disclosure in this application. It will be apparent to one of ordinary skill in the art that methods, devices, device elements, materials, procedures and techniques other than those specifically described herein can be applied to the practice of the invention as broadly disclosed herein without resort to undue experimentation. All art-known functional equivalents of methods, devices, device elements, materials, procedures and techniques specifically described herein are intended to be encompassed by this invention.

<u>Example1</u>: <u>Composite Stamps for Nanotransfer Printing</u>

[00105] The ability of the patterning devices of the present invention to provide composite stamps for nanotransfer printing applications was verified by experimental studies. Specifically, it is a goal of the present invention to provide

composite stamps capable of patterning large areas of a substrate surface with structures having selected lengths on the order of microns and 10's of nanometers. Further, it is a goal of the present invention to provide composite stamps for contact printing high resolution patterns exhibiting good fidelity and placement accuracy.

[00106] To achieve the aforementioned goals, composite stamps were fabricated using the methods of the present invention and used to generate patterns comprising monolayers of gold on substrates via nanotransfer printing (nTP). Specifically, large area composites stamps were generated and tested, comprising a thin (5 – 10 micron) PDMS layer in contact with a 25 micron thick polyimide (Kapton ®, DuPont) backing layer. In addition, large area composites stamps were generated and tested, comprising additional PDMS and/or polyimide layers. In one embodiment, a second PDMS layer having thickness of about 10 millimeters was attached to the polyimide layer. In another embodiment, a second polyimide layer was provided that was separated from the first polyimide layer by a thin (approximately 4 micron) PDMS layer. Use of additional PDMS and/or polyimide layers facilitated handling of the composite stamps and avoided curling after separation from the master relief pattern due shrinkage of the PDMS layer and/or mismatch of the coefficients of thermal expansion of the PDMS and polyimide layers.

[00107] Figure 4A shows a schematic illustration of an exemplary composite stamp used in this study and Figure 4B shows a corresponding cross section scanning electron microscopy image. As shown in Figure 4B, the relief pattern of the composite stamp is coated with a thin layer of gold. The relief pattern of this composite stamp corresponds to the source/drain level of an active matrix circuit for electronic paper displays consisting of 256 interconnected transistors arranged in a square array of over an area of 16 cm by 16 cm.

[00108] Distortions in composite stamps of the present invention were quantified by measuring with a microscope the misalignment at each transistor location between two successive prints, between one print and the stamp and the stamp used to print and between a stamp and its master relief pattern. Figures 5A and 5B show distortions that correspond to measurements of positions of features

on a composite stamp compared to those on its master relief pattern. These results include corrections for overall translation and rotational misalignment and isotropic shrinkage (about 228 ppm for stamps cured at 80 degrees Celsius and about 60 ppm for those cured at room temperature). The residual distortions are close to the estimated accuracy (approximately 1 micron) of the measurement method. These distortions include cumulative effects of (i) fabricating and releasing the stamp from its master relief pattern and (ii) printing (wetting the stamp) on an uneven substrate (the master has some relief features approximately 9 microns thick).

[00109] Another benefit of the composite stamp design of this example is its reduced tendency to sag mechanically in the recessed regions of the relief pattern, which can cause unwanted stamp-substrate contact that distorts a pattern transferred to a substrate surface. As an example, in the case of 60 micron wide lines separated by 60 microns (500 nanometer relief height), recessed areas of a regular single element PDMS stamp sag completely. In contrast, no sagging is observed for the same relief geometry on a composite stamp comprising four polymer layers: (1) 25 micron PDMS first layer, (2) 25 micron polyimide second layer, (3) 60 micron PDMS third layer, and (4) 25 micron polyimide fourth layer. Figs. 6A and 6B show top view optical micrographs that illustrate the reduced tendency for sagging of recessed areas in a composite stamp of the present invention. Figure 6A corresponds to a conventional single layer PDMS stamp and Figure 6B corresponds to a composite stamp of the present invention. The color uniformity in the recessed areas of the composite stamp (Figure 6B) suggests that the bowing is almost zero. Finite element modeling of the multilayer structure of the composite stamp indicates that the polyimide layer efficiently reduces the tendency of the stamp for sagging when the residual PDMS layer is thin.

[00110] Figure 7 shows the extent of shrinkage observed after curing a two layer stamp of the present invention comprising a thin PDMS layer in contact with a polyimide layer. As shown in Figure 7, composite stamps of the present invention undergo horizontal shrinkage equal to 0.2% or less and vertical shrinkage of 0.3% or less. The resistance to curing induced shrinkage provided by the composite stamp designs of the present invention minimizes distortions of the three-

dimensional relief pattern and contact surfaces and provides high resolution patterns exhibiting good fidelity with respect to the master relief pattern.

[00111] Figure 8 is a schematic illustration of a nanotransfer printing processes using a composite stamp of the present invention. As shown in Figure 8, the process begins with deposition of a gold coating on the surface of the composite stamp, thereby forming a discontinuous gold coating on the raised and recessed regions of the elastomeric first layer. Contacting the stamp to a substrate that supports a self assembled monolayer (SAM) designed to bond to the gold (e.g. a thiol terminated SAM) leads to strong adhesion between the gold and the substrate. Removing the stamp, to which gold only weakly adheres, transfers the gold on the raised regions of the stamp to the substrate.

[00112] Metal evaporation was performed with a Temescal electron beam system (BJD 1800) and deposition rates of 1 nm/s were employed. Pressures during evaporation were typically about 1×10^{-6} Torr or less. A deposition rate monitor was installed in position such that the rates could be established and stabilized before exposing the stamps or substrates to the flux of metal. The printing was performed in open air shortly after deposition. The stamps typically come into intimate contact with the substrates without applied pressure other than the force of gravity. In some cases small pressure applied by hand was used to initiate contact along an edge, which then proceeded naturally across the stamp-substrate interface. After a few seconds, the stamp was removed from contact with substrate to complete the printing.

[00113] Figures 9A-D show scanning electron micrographs of patterns of Ti/Au (2 nm / 20 nm) generated using composite stamps of the present invention. As illustrated in these figures, the methods and devices of the present invention are capable of generating a wide variety of patterns comprising structures having a range of physical dimensions. As shown in Figures 9A- D, the transferred Ti/Au patterns are largely free of cracks and other surface defects. Use of composite stamps of the present invention having a thickness less than 100 μm are preferred for some applications because the stress developed at the surface of the composite stamp when bent (during handling or initiation of contact) is small relative to

conventional PDMS stamps which are often substantially thicker (e.g. approximately 1 cm in thickness).

Example 2: Computer modeling of the Thermal Characteristics and Mechanical Properties of Composite Patterning Devices

[00114] The susceptibility of multilayer patterning devices of the present invention to distortions induced by polymerization during fabrication and mechanical stresses was evaluated by computation simulations. Specifically, the extent of deformation induced by polymerization during fabrication and the weight driven deformation of recessed regions was calculated for a four layer composite patterning device. These studies verified that composite patterning devices of the present invention exhibit enhanced stability with respect to polymerization induced shrinkage and weight driven sagging.

[00115] The extent of polymerization induced distortion was calculated and compared for two different composite pattern designs. First, a four layer composite patterning device **600**, shown schematically in Figure 10, was evaluated comprising a first 5 micron thick PDMS polymer layer **610**, a second 25 micron polyimide (Kapton ®) polymer layer **620**, a third 5 micron thick PDMS polymer layer **630** and a fourth 25 micron polyimide (Kapton ®) polymer layer **640**. Second, a two layer composite patterning device **700** shown schematically in Figure 11A was evaluated comprising a first 5 micron thick PDMS polymer layer **710**, a second 25 micron polyimide (Kapton ®) polymer layer **720**. A temperature change from 20 degrees Celsius to 80 degrees Celsius was used in both calculations. The Young's modulus and coefficient of thermal expansion of PDMS were assumed to be independent of temperature and equal to 3 MPa and 260 ppm, respectively. The Young's modulus and coefficient of thermal expansion of polyimide were assumed to be independent of temperature and equal to 5.34 GPa and 14.5 ppm, respectively.

[00116] Figure 10 shows the extent of distortion predicted during thermal induced polymerization calculated for the four layer composite patterning device **600**. As shown in Figure 10, no curling of the four layer pattern device is observed

upon polymerization. Figure 11A shows the extent of distortion during thermal induced polymerization calculated for the two layer composite patterning device **700**. In contrast to the results for the four layer patterning device, polymerization induced curling is observed for the two layer pattering device. Figures 11B and 11C provide plots of the radius of curvature after polymerization as a function of the thickness of the PDMS layer and the curing temperature, respectively, for the two layer pattering device.

[00117] The extent of vertical displacement of recessed regions of a four layer patterning device of the present invention was also examined via computer simulations. As shown in Figure 12A, the composite patterning device evaluated comprised two h-PDMS layers and two polyimide layers (Kapton ®). The thickness of the first h-PDMS layer was varied over the range of about 6 microns to about 200 microns. The thickness of the polyimide second layer was held constant at 25 microns, the thickness of the h-PDMS third layer was held constant at 5 microns, and the thickness of the polyimide fourth layer was held constant at 25 microns. Figure 12B shows a plot of the predicted vertical displacement in units of microns as a function of position along a recessed region about 90 microns in length. As shown in Figure 12B, distortions due to sagging less than about 0.2 microns is observed are observed for PDMS first layers having thicknesses equal to or less than 50 microns. In addition the extent of sagging observed for all embodiments examined was always less than about 0.1% of each the thickness evaluated. The results of these simulations suggest that four layer composite patterning devices of the present invention are unlikely to exhibit undesirable contact between recessed regions of the first layer and the substrate surface due to sagging of recessed regions of a relief pattern.

[00118] Figs. 13A-C shows the results of a computational study of horizontal distortion due to thermal/chemical shrinkage during polymerization for a two layer composite stamp of the present invention. Figure 13A is a schematic illustrating a two layer composite stamp comprising a PDMS layer of variable thickness operationally coupled to a 25 micron Kapton layer. Figure 13B is a plot of the predicted horizontal distortion as a function of the thickness of the PDMS first layer

in microns. Figure 13C is a plot of the predicted horizontal distortion as a function of the distance along the external surface of the PDMS first layer in millimeters. The modeling results suggest that the magnitude of distortions in planes parallel to the contact surfaces on the external surface of the PDMS first layer due to polymerization is directly proportional to the PDMS first layer thickness. In addition, the modeling results show that distortions in planes parallel to the contact surfaces on the external surface of the PDMS first layer due to polymerization are largely confined to the edges of the stamp when the thickness of the PDMS first layer is decreased.

[00119] Example 3: Fiber Reinforced Composite Patterning Devices

The present invention includes composite pattering devices comprising one or more composite polymer layers, including polymer layers having fiber materials providing beneficial mechanical, structural and/or thermal properties. Composite patterning devices of this aspect of the present invention include designs wherein fibers are integrated into and/or between polymer layers in geometries selected to provide a net flexural rigidity that minimizes distortion of the relief features of a relief pattern and which provide patterning devices capable of generating patterns exhibiting good fidelity and placement accuracy on substrate surfaces. Furthermore, composite patterning devices of this aspect of the present invention include designs wherein fibers are integrated into and/or between polymer layers in geometries selected to minimize expansion or contraction of polymer layers due changes in temperature and/or to facilitate physical manipulation of patterning devices of the present invention, for example by adding to the thickness of these devices.

[00120] To evaluate verify the utility of integrated fiber materials in composite patterning devices of the present invention, a pattering device comprising a plurality of glass fiber reinforced polymer layers was designed. Figures 14A and14B provide schematic diagrams illustrating a fiber reinforced composite stamp of the present invention. Figure 14A provides a cross sectional view and Figure 14B provides a perspective view. As shown in Figures 14A and 14B the fiber reinforced composite stamp **900** comprises a first layer **905** comprising PDMS and having a relief pattern

with relief features of selected physical dimensions, a second layer **910** comprising a composite polymer having an array of fine glass fibers in a first selected orientation, a third layer **915** comprising a composite polymer having a mesh of larger glass fibers in a second selected orientation, a fourth layer **920** comprising a composite polymer having a mesh of large glass fibers in a third selected orientation and a fifth layer **925** comprising a composite polymer having an array of fine glass fibers in a fourth selected orientation. First layer **905** has a low Young's modulus and is capable of establishing conformal contact between its contact surface(s) and a range of surfaces including contoured, curved and rough surfaces. Second layer **910** is a composite polymer layer wherein the addition of an array of fine glass fibers in a selected orientation provides mechanical support to the roof of the relief features of first layer **905**, thereby minimizing distortion of the relief pattern on first layer **905** upon formation of conformal contact with a substrate surface. Third and fourth layers **915** and **920** provide an overall thickness of the fiber reinforced composite stamp **900** such that it can be easily manipulated, cleaned and/or integrated into a stamping device. Incorporation of glass fibers into second, third, fourth and/or fifth layers **910, 915, 920** and **925** also provide a means of selecting the net flexural rigidity of the fiber reinforced composite stamp and provides a means of selecting the Young's modulus of individual layers in patterning devices of the present invention. For example, selection of the composition, orientation, size and density of fibers in second, third, fourth and/or fifth layers **910, 915, 920** and **925** may provide a net flexural rigidity useful for generating patterns exhibiting good fidelity and placement accuracy on substrate surfaces. Second, third, fourth and fifth layers **910, 915, 920** and **925** may comprise fiber reinforced composite layers of a polymer having a low Young's modus or polymer having a high Young's modus. Optionally, fiber reinforced composite stamp **900** may further comprise one or more additional high or low Young's modulus polymer layers, include additional composite polymer layers having fiber materials.

[00121] Figure 14C provides a schematic diagram illustrating first **930**, second **935**, third **940** and fourth **945** selected orientations corresponding to second, third, fourth and fifth layers **910, 915, 920** and **925**, respectively, of fiber reinforced composite stamp **900.** As shown in Figure 14C, first selected orientation **930** provides an array of longitudinally aligned fine glass fibers in the second layer **910**

arranged along axes that are orthogonal to the longitudinally aligned fine glass fibers in the fourth selected orientation **945** of the fifth layer **925**. Second and third selected orientations provide fiber meshes wherein two sets of fibers are aligned and interwoven along orthogonal axes. Additionally, fiber meshes corresponding to second and third selected orientations **935** and **940** provide fibers orientations that are orthogonal to each other, as shown in Figure 14C. Use of the fiber mesh orientations shown in Figure 14C minimizes anisotropy in the in plane mechanical properties of polymer layers and patterning devices of the present invention.

[00122] Figure 15 provides an optical image of a composite polymer layer bonded to a PDMS layer. As shown in Figure 15, the composite polymer layer **971** comprises a glass fiber mesh and the PDMS layer **972** does not have any integrated fiber materials.

[00123] Referring again to Figure 14A, the stamp design shown provides an arrangement of fiber reinforced layers that is symmetrical about design axis **960**. Use of a second layer **910** and a fifth layer **925** having substantially the same thermal expansion coefficient and a third layer **915** and a fourth layer **920** having substantially the same thermal expansion coefficient provides a fiber reinforced composite stamp **900** having a substantially symmetrical distribution of thermal expansion coefficients about layer alignment axis **980**. This is particularly true if first layer is relatively thin compared to the sum of second, third, fourth and fifth layers, for example preferably less than 10% for some applications and more preferably less than 5% for some applications. As described above, use of device configurations in the present invention providing a substantially symmetrical distribution of thermal expansion coefficients about layer alignment axis **980** orthogonal to a plane containing the contact surface(s) is useful for providing thermally stable patterning devices that exhibit minimal pattern distortions induced by changes in temperature. Further more, this symmetrical arrangement minimizes relief pattern distortions induced during curing, for example pattern distortions caused of curling of polymer layers during curing.

[00124] The use of fiber materials allows for integration of a wide range of materials having useful mechanical and thermal properties, including brittle

material, into patterning devices and polymer layers of the present invention in a manner that preserves their ability of to exhibit flexibility allowing for establishment of conformal contact with rough and contoured substrate surfaces, such as surfaces having a large radius of curvature. For example, SiO_2 is a material that is very brittle in the bulk phase. However, use of SiO_2 fibers, fiber arrays and fiber meshes that are relatively thin (e.g. have diameters less than about 20 microns) allow structural reinforcement of polymer layers and enhances net flexural rigidity while maintaining their ability to be flexed, stretched and deformed. Furthermore, SiO_2 exhibits good adhesion to some polymers, including PDMS. Carbon fibers are another class of material that integration into polymer layers leads to substantially enhancement of flexural rigidity and Young's modulus while allowing for device flexibility useful for establishing good conformal contact with a range of surface morphologies.

[00125] Any composition of fiber material and physical dimensions of fiber materials, may be used in fiber reinforced polymer layers of the present invention that provides patterning device and polymer layers exhibiting beneficial mechanical, structural and thermal properties. Fiber materials useful in the present composite patterning devices include, but are not limited to, fibers comprising glass including oxides such as SiO_2, Al_2O_2, B_2O_3, CaO, MgO, ZnO, BaO, Li_2O, TiO_2, ZrO_2, Fe_2O_3, F_2, and Na_3O / K_2O, carbon, polymers such as aramid fiber and dyneema, metals and ceramics or mixtures of these materials may be incorporated into patterning devices of the present invention. Fiber materials exhibiting good adhesion to the polymer comprising the layer it is integrated into are preferred materials for some applications. Fibers having lengths ranging from about 1 to about 100 microns are useful in fiber reinforced composite patterning devices of present invention, preferably about 5 to about 50 microns for some applications. Fibers having diameters ranging from about 0.5 microns to about 50 microns are useful in fiber reinforced composite patterning devices of present invention, preferably about 5 to about 10 microns for some applications.

[00126] Composite layers in fiber reinforced patterning devices of the present invention may have any selected arrangement of fibers providing patterning devices with useful mechanical and thermal properties. Use of fiber arrangements

characterized by a high fiber volume fraction, for example a fiber volume fraction greater than about 0.7, is useful in composite layers (e.g. layer **910** in Figure 14A) providing support to relief features and recessed areas, including roof support, to in relief patterns of low modulus layers having one or more contact surfaces. Use of fiber arrangements characterized by a lower fiber volume fraction, for example a fiber volume fraction less than about 0.5, is useful in composite layers (e.g. layers **915** and **920** in Figure 14A) providing a desirable net stamp thickness in order to maintain the flexibility of the fiber reinforced composite patterning device. As exemplified in the schematic diagrams shown in Figures 14A – 14C, use of a plurality of composite layers having different selected fiber orientations is useful in for providing fiber reinforced composite patterning devices having isotropic mechanical properties with respect to deformation along axis that are orthogonal to a plane containing the contact surface.

[00127] In addition to their in addition to their structural and mechanical properties, fiber materials for fiber reinforced composite patterning devices of the present invention may also be selected on the basis of their optical and/or thermal properties. Use of fibers having a refractive index equal to or similar to the polymer material in which it is integrated into (i.e. matched to within 10%) is useful for providing optically transparent composite polymer layers. For example, the index of refraction of SiO_2 fiber can be tuned to match the index of refraction of PDMS (typically between 14. to 1.6) to make a highly transparent composite polymer layer. Matching refractive index of fiber and polymer materials in a given composite polymer layer is particularly useful for fiber reinforced composite photomasks of the present invention. In addition, selection of a fiber material having a thermal expansion coefficient equal to or similar to the polymer material in which it is integrated into (i.e. matched to within 10%) is useful for providing thermal stable fiber reinforced composite patterning devices.

<u>Example 4</u>: <u>Composite Soft Conformal Photomask</u>

[00128] The present invention includes composite patterning devices comprising photomasks capable of establishing and maintaining conformal contact with the surface of a substrate undergoing processing with electromagnetic radiation. An advantage of composite conformal photomasks of the present

invention is that they are able to conform to a wide range of substrate surface morphologies without significantly changing the optical properties, such as two dimensional transmission and absorption properties, of the photomask. This property of the present invention provides photomasks capable of transmitting electromagnetic radiation having well defined two dimensional spatial distributions of intensities, polarization states and/or wavelengths of electromagnetic radiation on selected areas of a substrate surface, thereby allowing fabrication of patterns on substrate exhibiting good fidelity and placement accuracy.

[00129] Figure 16 provides a schematic diagram of a composite soft conformal photomask of the present invention. As shown in Figure 16, the composite soft conformal photomask **1000** comprises a first polymer layer **1005** having a low Young's modulus and having a contact surface **1010**, a patterned layer photomasking layer **1015** comprising a plurality of optically transmissive **1017** and nontransmissive regions **1016**, and a second polymer layer **1020** having high Young's modulus and an external surface **1025**. In a useful embodiment, the first polymer layer comprises PDMS and the second polymer layer comprises polyimide. Transmissive regions **1017** at least partially transmit electromagnetic radiation exposed to external surface **1025** and nontransmissive regions **1016** at least partially attenuate the intensities of electromagnetic radiation exposed to external surface **1025**, for example by reflecting, absorbing or scattering the electromagnetic radiation. In the embodiment shown in Figure 16, nontransmissive regions **1016** are reflective thin aluminum films in contact with a substantially transparent Ti/SiO_2 layer. In this arrangement, substantially transparent regions between reflective thin aluminum films are transmissive regions.

[00130] To provide patterning on a substrate surface, the composite soft conformal photomask **1000** is brought into contact with a substrate surface such that the contact surface **1010** of first polymer layer **1005** establishes conformal contact with the substrate surface. Electromagnetic radiation having first two dimensional distributions of intensities, polarization states and/or wavelengths is directed onto external surface **1025** of second polymer layer **1020** of composite soft conformal photomask **1000**. Reflection, absorption and/or scattering by nontransmissive regions **1016** generates transmitted electromagnetic radiation

characterized by different two dimensional distributions of intensities, polarization states and/or wavelengths. This transmitted electromagnetic radiation interacts with the substrate surface and generates physically and/or chemically modified regions of the substrate surface. Patterns are fabricated either by removing at least a portion of the chemically and/or physically modified regions of the substrate or by removing at least a portion of the substrate that is not chemically and/or physically modified.

[00131] Figure 17A shows an optical image of a composite soft conformal photomask of the present invention and Figure 17B shows an optical image of exposed and developed photo-resist patterns on a silicon substrate. As shown in Figure 17A, the composite soft conformal photomask **1100** has a 5 millimeter thick handle **1105** providing a border which allows easy manipulation, cleaning and integration of the photomask with other processing instrumentation. A comparison of Figures 17A and 17B demonstrate that patterns having high fidelity are generated using the composite soft conformal photomask.

[00132] Figure 18 provides a process flow diagram illustrating a method of making a composite soft conformal photomask of the present invention. As shown in process step A of Figure 18, a thin aluminum layer is deposited onto the internal surface of a high Young's modulus polymer via electron beam evaporation. As shown in process step B of Figure 18, a layer of photoresist is deposited on the aluminum layer, for example by spin coating, and is patterned, for example using conventional photolithography. This patterning step generates a patterned photomasking layer comprising thin aluminum films having selected physical dimensions and positions. As shown in process step C of Figure 18, a thin film of Ti/SiO_2 is deposited on the aluminum patterned photomasking layer and exposed regions of the internal surface of the high Young's modulus polymer layer. Use of a Ti/SiO_2 layer is useful for promoting adhesion to a PDMS layer in subsequent processing steps. As shown in process step D of Figure 18, a substantially flat silicon substrate is treated with a nonstick self assembled monolayer and a thin layer of PDMS is spin coated on top of the self assembled monolayer. Use of the self assembled monolayer in this aspect of the invention is important for preventing irreversible bonding of the PDMS layer to the silicon surface and to avoid damage

of the PDMS layer upon separation from the silicon substrate. As shown in process step E of Figure 18, the Ti/SiO_2 layer of the composite structure comprising high Young's modulus layer and the pattern photomasking layer is brought into contact with the PDMS-coated silicon substrate. A force is applied to the external surface of the high Young's modulus layer and the PDMS layer is cured at a temperature between 60 – 80 degrees Celsius for a few hours. Finally, the PDMS layer is separated from the silicon substrate thereby forming the composite soft conformal photomask.

Example 4: Lock and Key Registration System Using Patterning Agent

[00133] The present invention provides methods and pattering devices and/or substrate surfaces having specific relief patterns, such as alignment channels, troughs and/or grooves, useful for providing proper registration and alignment of patterning devices and substrate surfaces. Particularly, use of "lock and key" alignment systems comprising complimentary (i.e. mating) relief features and recessed regions is useful in the present invention because engagement of complementary features constrains the possible relative orientations of the contact surface of a patterning device and a substrate surface. The ability to constrain the relative orientation of these elements is particularly useful for fabricating devices and device arrays with good placement accuracy over large substrate areas.

[00134] In one aspect, the present invention includes alignment systems using a patterning agent for establishing and maintaining a selected spatial alignment between the contact surface of a patterning device, such as the contact surface of a composite patterning device or the contact surface of a single layer patterning device, and a selected region of the substrate surface. In the context of this description, the term "patterning agent" refers to one or more materials that are provided between at least a portion of the contact surface of a patterning devices and a substrate surface undergoing processing. In this aspect of the present invention, the patterning agent functions to facilitate proper alignment and engagement of complementary relief features and recessed regions in a manner resulting good registration of these elements. Patterning agents of the present invention may provide functionality other than or in addition to facilitating proper

alignment of a patterning device and a substrate surface. In one embodiment, patterning agents of the present invention comprise an optical filtering medium for a photomask of the present invention. In another embodiment, patterning agents comprise a transfer material that is molded onto a substrate surface, for example a prepolymer material that is molded into a pattern embossed on the substrate surface upon exposure to electromagnetic radiation or upon increasing temperature. Patterning agents of the present invention may also provide a multifunctional character such as a combination of facilitating alignment of a contact surface of a patterning device and a substrate surface undergoing processing and providing optical filtering and/or a transfer material for patterning a substrate surface.

[00135] In one embodiment, patterning agents of the present invention act as lubricants by reducing friction generated between a mating contact surface and substrate surface pair of an alignment system, such as a lock and key registration system. By reducing friction, the patterning agent allows the patterning device and the substrate to establish conformal contact and move relative to each other, thereby sampling a range of possible relative orientations. In this aspect of the present invention, additional mobility provided by the patterning agent allows the patterning device and substrate surface to realize a stable, selected relative orientation characterized by effective coupling between complementary relief features and recessed regions on the mating surfaces. Effective patterning agents facilitate establishing correct registration without interfering with establishment of conformal contact. Useful patterning agents include fluids, such as liquids and colloids, thin films and particulate materials. Exemplary patterning agents include Optical Brightener, Benetex OB-EP from Mayzo, Parker ink, Water soluble black wooden dye Powerder from Constantines Wood Center.

[00136] Patterning devices of this aspect of the present invention have a contact surface having a plurality of recessed regions or relief features having shapes and physical dimensions that are complementary to recessed regions or relief features on a substrate surface undergoing processing. Patterning devices of this aspect of the present invention also have a means for introducing the patterning agent into a least a part of the region between the contact surface and the substrate

surface. Means for introducing the patterning agent can be a fluidic channel, groove or may involve wetting the contact surface or substrate surface prior to establishing conformal contact, for example using a dipping system. To achieve registration, the patterning device and substrate surface are gradually brought into contact by establishing an appropriate force, for example a force directed orthogonal to a plane containing at least a portion of the contact surface. Optionally, alignment may involve movement of the mating surface of the patterning device and the substrate surface in other directions, for example by lateral movement of the surfaces.

[00137] In another aspect, the patterning agent acts as the optical filtering medium for a conformable photomask. In this aspect of the invention, the composition of the patterning agent is selected such it that it absorbs, scatters, reflects or otherwise modulates some property of electromagnetic radiation directed onto the photomask, thereby selectively adjusting the intensities, wavelengths and polarization states of light transmitted onto a substrate surface undergoing patterning. In one embodiment, for example, the patterning agent is provided between a conformable photomask having a relief pattern and the external surface of a substrate. Conformal contact between the photomask and the external surface of the substrate generates a series of spaces occupied by the patterning agent that are defined by the relief features and recessed regions of the relief pattern. These spaces may comprise a series of channels, chambers, apertures, grooves, slits and/or passages positioned between the photomask and the external surface of the substrate. The shapes and physical dimensions of the relief features and recessed regions of the photomask determine optical thicknesses of the patterning agent present in the spaces between the photomask and the substrate surface. Selection of the relief pattern geometry and composition of the patterning agent, therefore, provides a means of modulating transmitted electromagnetic radiation to achieve selected two dimensional spatial distributions of the intensities, wavelengths and/or polarization states of light transmitted onto the substrate surface. This aspect of the invention is particularly useful for patterning substrate surfaces having a layer of photosensitive material deposited on their external surfaces.

[00138] Advantages of this patterning approach of the present invention include (i) it is compatible with the types of composite patterning devices described throughout this application, (ii) the patterning agent can have low viscosity, which enables it to flow rapidly and effectively as the patterning device is brought into contact with the patterning agent (which helps to push most of the patterning agent out of the regions that correspond to raised areas on the patterning device), (iii) it lubricates the interface between the contact surface (or coated contact surface) and the substrate surface (or coated substrate surface), (iv) it does not alter the stretchability of the patterning device, which is an important characteristic, especially if the patterning device has to stretch to match the lock and key features (due to slight deformations in the substrate, for example) and (v) it can pattern conventional photoresists whose processing conditions and uses are well established for many important electronic and photonic applications.

[00139] Figures 19A and 19B provide schematic diagrams showing alignment systems using a patterning agent for aligning a photomask and substrate. Referring to Figures 19A and 19B, the alignment system **1300** of the present invention comprises a conformable photomask **1305** having a contact surface **1306**, a substrate **1310** with an external surface **1313** undergoing processing and a patterning agent **1315** disposed between the contact surface **1306** and external surface **1313**. In the embodiment shown in Figures 19A and 19B, external surface **1313** undergoing processing is coated with a photosensitive layer **1314**, such as a photoresist layer. In the design shown in Figure 19A, conformable photomask **1300** comprises a first polymer layer, for example a PDMS layer, having a plurality of recessed regions **1320** having shapes and physical dimensions that are complementary to relief features **1325** present on external surface **1313** undergoing processing. In the design shown in Figure 19B, conformable photomask **1300** comprises a first polymer layer, for example a PDMS layer, having a plurality of relief features **1340** having shapes and physical dimensions that are complementary to recessed regions **1345** present on external surface **1313** undergoing processing. Relief features and recessed regions of this aspect of the present invention may have any pair of complementary shapes including, but not limited to, having shapes selected from the group consisting of pyramidal,

cylindrical, polygonal, rectangular, square. conical, trapezoidal, triangular, spherical and any combination of these shapes.

[00140] Optionally, conformable photomask **1305** may further comprise additional relief features **1308** and recessed regions **1307** having selected shapes and physical dimensions. As shown in Figures 19A and 19B, conformal contact of photomask **1305** and external surface **1313**, generates a plurality of spaces occupied by patterning agent **1315**, because substrate **1310** is not provided with relief features and recessed regions complementary to additional relief features **1308** and recessed regions **1307**. In one embodiment, patterning agent **1315** is a material that absorbs, reflects or scatters electromagnetic radiation directed onto photomask **1305** and, therefore, the shapes and physical dimensions of relief features **1308** and recessed regions **1307** establishes two dimensional spatial distributions of intensities, wavelengths and/or polarization states of electromagnetic radiation transmitted to photosensitive layer **1314** on external surface **1313**. In this manner, selected regions of photosensitive layer **1314** may be illuminated with selected intensities of electromagnetic radiation having selected wavelengths and polarization states, and selected regions of photosensitive layer **1314** may be shielded from exposure to electromagnetic radiation having selected wavelengths and polarization states. This aspect of the present invention is useful for patterning photosensitive layer **1314** by exposure to electromagnetic radiation characterized by a selected two dimensional spatial distribution of intensities capable of generating chemically and/or physically modified regions of photosensitive layer **1314** corresponding to a desired pattern. In one embodiment, the photomask **1305** is a phase only photomask which is substantially transparent. In this embodiment, it only forms an amplitude photomask when the patterning agent is present between contact surface **1306** and external surface **1313**

[00141] In another embodiment, patterning agent **1315** is a transfer material for molding patterns onto the substrate surface. In this embodiment, therefore, the shapes and physical dimensions of relief features **1308** and recessed regions **1307** establishes features of a pattern that is embossed onto photosensitive layer **1314** on external surface **1313**. Embodiments of this aspect of the present invention, are

also useful for patterning a substrate surface via molding patterns on external surface **1313** directly (i.e. without photosensitive layer **1314** present).

[00142] Optionally, conformable photomask **1305** is a composite photomask further comprising additional polymer layers, such as high Young's modulus layers, composite polymer layers and low Young's modulus layers (not shown in Figures 19A and 19B). As discussed throughout the present application, patterning device of the present invention having one or more additional polymer layers provides beneficial mechanical and/or thermal properties. Patterning devices of this Example of the present invention, however, do not have to be composite patterning devices.

[00143] To generate a pattern on the surface of substrate **1310**, patterning agent **1315** is provided between the contact surface **1306** of conformable photomask **1305** and external surface **1313**, and the contact surface **1306** and external surface **1313** are brought into conformal contact. Patterning agent **1315** lubricates the interface between the first polymer layer of conformable photomask **1305** and the photosensitive layer **1314** on external surface **1313**. The decrease in friction caused by the presence of the patterning agent **1315** enables the contact surface **1306** to align with the external surface **1313** such that the relief features (**1325** or **1340**) to optimally engage with recessed regions (**1320** or **1345**). Optimal alignment is achieved by providing a gradual force that brings the mating surface together, such as a force directed along an axis orthogonal to the contact surface (schematically represented by arrows **1380**). Optionally, contact surface **1306** and external surface **1313** may be moved laterally (along an axis parallel to axis **1390**) to enhance establishing of optimal engagement of recessed regions (**1320** or **1345**) and relief features (**1325** or **1340**).

[00144] The conformable photomask **1305** is illuminated with electromagnetic radiation, and transmits electromagnetic radiation having a selected two dimensional spatial distribution of intensities, wavelengths and/or polarization states to photosensitive layer **1314**. For example, patterning agent **1315** present in the region between relief features **1308** and recessed regions **1307** and external surface **1313** may absorb, scatter or reflect incident electromagnetic radiation,

thereby providing spatially resolved optical filtering functionality. For example, in one embodiment patterning agent **1315** absorbs UV electromagnetic radiation, thus creating contrast for patterning the photosensitive layer **1314** with ultraviolet light. The transmitted electromagnetic radiation interacts with portions of photosensitive layer **1314** thereby generating patterns of chemically and/or physically modified regions. After exposure to sufficient electromagnetic radiation for a given application, conformable photomask **1305** and substrate **1310** are separated, and photosensitive layer **1314** is developed by either removing at least a portion of chemically and/or physically modified regions of photosensitive layer **1314** or by removing at least a portion of photosensitive layer **1314** that is not chemically and/or physically modified.

[00145] Figure 20 provides a schematic diagram illustrating an exemplary patterning method of the present invention using a patterning agent that comprises an optical medium (or ink) of conformable photomask. As shown in Figure 20, a substrate having a photoresist layer on its external surface is provided. The photoresist layer is contacted with a patterning agent comprising an ink and a conformable photomask is brought into conformal contact with the substrate. As shown in Figure 20, the pattern agent is present in spaces defined by the relief pattern of the conformable photomask. The conformable photomask is illuminated with electromagnetic radiation, and the pattern agent modulates the intensity of the electromagnetic radiation transmitted to the photoresist layer. As illustrated in Figure 20, the conformable photomask is them removed and the photoresist layer is developed, thereby generating a pattern on the substrate surface defined by the optical thicknesses of pattern agent present between the photomask and substrate.

We claim:

1. A composite patterning device for generating a pattern on a substrate surface, said device comprising:

   a first polymer layer comprising a three-dimensional relief pattern having at least one contact surface disposed thereon, said first polymer layer having a low Young's modulus and having an internal surface opposite said contact surface; and

   a second polymer layer having an internal surface and an external surface; said second polymer layer having a high Young's modulus; wherein said first polymer layer and said second polymer layer are arranged such that a force applied to the external surface of said second polymer layer is transmitted to said first polymer layer;

   wherein said composite patterning device is capable of establishing conformal contact between at least a portion of said contact surface of said first polymer layer and said substrate surface.

2. The device of claim 1 wherein said internal surface of said first polymer layer is in contact with said internal surface of said second polymer layer.

3. The device of claim 1 wherein said first polymer layer and said second polymer layer are connected by a connecting layer positioned between said internal surface of said first polymer layer and said internal surface of said second polymer layer.

4. The device of claim 1 wherein said connecting layer comprises a thin metal layer.

5. The device of claim 1 wherein said first polymer layer and said second polymer layer are arranged such that a force applied to the external surface

of said second polymer layer is transmitted to at least a portion of the contact surface of said first polymer layer.

6. The device of claim 1 wherein said three-dimensional relief pattern has a plurality of contact surfaces.

7. The device of claim 6 wherein said contact surfaces are in substantially the same plane.

8. The device of claim 6 wherein at least a portion of said contact surfaces are in different planes.

9. The device of claim 1 wherein the thickness of said first polymer layer is selected from the range of about 1 micron to about 100 microns.

10. The device of claim 1 wherein the thickness of said first polymer layer is about 5 microns.

11. The device of claim 1 wherein the thickness of said second polymer layer is selected from the range of about 10 microns to about 100 microns.

12. The device of claim 1 wherein the thickness of said second polymer layer is about 25 microns.

13. The device of claim 1 wherein the ratio of the thickness of the first polymer layer and the thickness of the second polymer layer is selected from the range of about 1 to about 10.

14. The device of claim 1 wherein said second polymer layer has a Young's modulus selected from the range of about 1 GPa to about 10 GPa.

15. The device of claim 1 wherein said first polymer layer has a Young's modulus selected from the range of about 1 MPa to about 10 MPa.

16. The device of claim 1 wherein said first polymer layer has a Young's modulus of about 3 MPa.

17. The device of claim 1 wherein said first polymer layer, second layer or both further comprising a fiber material.

18. The device of claim 17 wherein said fiber material is selected from the group consisting of glass fiber, carbon fiber, metal fiber, a ceramic fiber and polymer fiber.

19. The device of claim 1 wherein said second polymer layer is selected from the group consisting of a thermoset layer, a polyimide, a thermoplastic layer and a composite polymer layer.

20. The device of claim 1 wherein said second polymer layer comprises a polymer having a coefficient of thermal expansion less than or equal to about 14.5 ppm.

21. The device of claim 1 wherein said first polymer layer is an elastomer layer.

22. The device of claim 1 wherein said first polymer layer comprises poly(dimethylsiloxane) or h-poly(dimethylsiloxane).

23. The device of claim 1 wherein said first polymer layer is a composite polymer layer.

24. The device of claim 1 further comprising a third polymer layer position between said first and second polymer layers, wherein said third polymer is a composite polymer layer comprising a fiber material.

25. The device of claim 1 wherein said composite patterning device has a flexural rigidity selected from the range of about 1×10^{-7} Nm to about 1×10^{-5} Nm.

PCT/US05/14449

26. The device of claim 1 wherein said relief pattern occupies an area selected from the range of about 10 cm^2 to about 260 cm^2.

27. The device of claim 1 wherein said relief pattern comprises a plurality of relief features exhibiting dimensions selected over the range of about 10,000 nanometers to about 50 nanometers.

28. The device of claim 1 wherein said relief pattern comprises a plurality of relief features exhibiting dimensions selected over the range of about 1000 nanometers to about 50 nanometers.

29. The device of claim 1 wherein said first polymer layer is a continuous, unitary layer.

30. The device of claim 1 wherein said first polymer layer is a discontinuous layer.

31. The device of claim 30 wherein said three-dimensional relief pattern comprises a plurality of independent relief features, wherein said independent relief features are in contact with said second polymer layer.

32. The device of claim 1 further comprising a third polymer layer having an internal surface and an external surface, wherein said first, second and third polymer layers are arranged such that a force applied to said external surface of said third polymer layer is transmitted to said first polymer layer.

33. The device of claim 32 wherein said internal surface of said third polymer layer is in contact with said external surface of said second polymer layer.

34. The device of claim 32 wherein said second polymer layer and said third polymer layer are connected by a connecting layer positioned between said external surface of said second polymer layer and said internal surface of said third polymer layer.

PCT/US05/14449

35. The device of claim 32 wherein said third polymer layer has a low Young's modulus.

36. The device of claim 32 wherein said third polymer layer has a Young's modulus selected from the range of about 1 MPa to about 10 MPa.

37. The device of claim 32 wherein the thickness of said third polymer layer is selected from the range of about 1 micron to about 100 microns.

38. The device of claim 32 wherein the thickness of the third polymer layer is within about 10% of the thickness of the first polymer layer.

39. The device of claim 32 wherein the thermal expansion coefficient of said first polymer layer is within about 10% of the thermal expansion coefficient of said third polymer layer.

40. The device of claim 32 wherein said third polymer layer is an elastomeric layer.

41. The device of claim 32 wherein said third polymer layer comprises poly(dimethylsiloxane) or h-poly(dimethylsiloxane).

42. The device of claim 32 wherein said third polymer layer comprises a means of evenly distributing an applied pressure to said contact surface.

43. The device of claim 32 further comprising a fourth layer having an internal surface and an external surface, wherein said first, second, third and fourth polymer layers are arranged such that a force applied to said external surface of said fourth polymer layer is transmitted to said first polymer layer.

44. The device of claim 43 wherein said internal surface of said fourth polymer layer is in contact with said external surface of said third polymer layer.

45. The device of claim 43 wherein said third polymer layer and said fourth polymer layer are connected by a connecting layer positioned between said external surface of said third polymer layer and said internal surface of said fourth polymer layer.

46. The device of claim 43 wherein said fourth polymer layer has a high Young's modulus.

47. The device of claim 43 wherein said fourth polymer layer has a Young's modulus selected from the range of about 1 GPa to about 10 GPa.

48. The device of claim 43 wherein thickness of said fourth polymer layer is selected from the range of about 10 microns to about 100 microns.

49. The device of claim 43 wherein the thickness of said fourth polymer layer is within about 10% of the thickness of said second polymer layer.

50. The device of claim 43 wherein the thermal expansion coefficient of said fourth polymer layer is within about 10% of the thermal expansion coefficient of said second polymer layer.

51. The device of claim 43 wherein said fourth layer comprises a material selected from the group consisting of:

    a polymer;
    a glass;
    a ceramic; and
    a metal.

52. The device of claim 1 further comprising an actuator connected to said external surface of said second polymer layer, wherein said actuator is capable of providing a force to said external surface of said second polymer layer.

53. The device of claim 32 further comprising an actuator connected to said external surface of said third polymer layer, wherein said actuator is capable of providing a force to said external surface of said third polymer layer.

54. The device of claim 43 further comprising an actuator connected to said external surface of said fourth polymer layer, wherein said actuator is capable of providing a force to said external surface of said fourth polymer layer.

55. The device of claim 1 comprising a stamp, a mold or a photomask.

56. The device of claim 1 wherein said composite patterning device transmits electromagnetic radiation in the ultraviolet region of the electromagnetic spectrum, the visible region of the electromagnetic spectrum or both the ultraviolet region and visible region of the electromagnetic spectrum.

57. The device of claim 1 wherein said composite patterning device transmits a pattern of electromagnetic radiation having a selected two dimensional spatial distribution of intensities.

58. The device of claim 1 wherein the composite patterning device has a net thermal expansion coefficient that is within 10% of the thermal expansion coefficient of said substrate.

59. A composite patterning device for generating a pattern on a substrate surface, said device comprising:

a first layer comprising a three-dimensional relief pattern having at least one contact surface disposed thereon, said first layer having a low Young's modulus and having an internal surface opposite said contact surface;

a second layer having an internal surface and an external surface; said second layer having a high Young's modulus; and

a third layer having an internal surface and an external surface; wherein said first, second and third polymer layers are arranged such that a force applied to the external surface of said third polymer layer is transmitted to said first polymer layer; and

wherein the thicknesses and thermal expansion coefficients of said first and third layers are selected to provide a substantially symmetrical distribution of the coefficients of thermal expansion about the center of said patterning device along a layer alignment axis extending through said patterning device, and wherein said composite patterning device is capable of establishing conformal contact between at least a portion of said contact surface of said first layer and said substrate surface.

60. The device of claim 59 wherein said internal surface of said first layer is in contact with said internal surface of said second layer and wherein said external surface of said second layer is in contact with said internal surface of said third layer.

61. The device of claim 59 wherein said first polymer layer and said second polymer layer are connected by a connecting layer positioned between said internal surface of said first polymer layer and said internal surface of said second polymer layer and wherein said third polymer layer and said fourth polymer layer are connected by a connecting layer positioned between said external surface of said third polymer layer and said internal surface of said fourth polymer layer.

62. The device of claim 59 wherein said layer alignment axis is oriented orthogonal to a plane containing at least one contact surface.

63. A patterning device for generating a pattern on a substrate surface, said device comprising:

PCT/US05/14449

an polymer layer comprising a three-dimensional relief pattern and a base, wherein said three-dimensional relief pattern has at least one contact surface disposed thereon, wherein said base has an external surface positioned opposite to said contact surface, wherein said contact surface is orthogonal to a layer alignment axis extending through said layer, and wherein the Young's modulus of said polymer layer varies continuously along said layer alignment axis from a said contact surface to said external surface.

wherein said patterning device is capable of establishing conformal contact between at least a portion of said contact surface and said substrate surface.

64. The device of claim 63 wherein the Young's modulus of said polymer layer varies continuously along said layer alignment axis from a low modulus value at said contact surface to a high modulus value at a mid point along said layer alignment axis between said contact surface and said external surface.

65. The device of claim 63 wherein the Young's modulus of said polymer layer varies continuously from said high modulus value at a mid point along said layer alignment axis to a low modulus value at said external surface.

66. The device of claim 63 wherein said polymer layer has a substantially symmetrical distribution of the coefficients of thermal expansion about the center of said patterning device along said layer alignment axis.

67. A method of generating a pattern on a substrate surface, said method comprising the steps of:

providing a composite patterning device comprising:

a first polymer layer comprising a three-dimensional relief pattern having at least one contact surface disposed thereon, said first polymer layer having a low Young's modulus and having a internal surface opposite said contact surface; and

a second polymer layer having an internal surface and an external surface; said second polymer layer having a high Young's modulus; wherein said first polymer layer and said second polymer layer are arranged such that a force applied to the external surface of said second polymer layer is transmitted to said first polymer layer;

depositing a transfer material onto said contact surface of said first polymer layer, thereby generating a layer of transfer material on the contact surface;

contacting said composite patterning device and said substrate surface in a manner establishing conformal contact between at least a portion of said contact surface and said substrate surface, wherein said layer of transfer material is exposed to said substrate surface; and

separating said composite patterning device and said substrate surface, thereby transferring at least a portion of said transfer material to said substrate surface and generating said pattern on said substrate surface.

68. The method of claim 67 wherein said depositing step comprises depositing said transfer material onto said contact surface via vapor deposition.

69. The method of claim 67 wherein said depositing step comprises depositing said transfer material onto said contact surface via sputtering deposition.

70. The method of claim 67 wherein said depositing step comprises depositing said transfer material onto said contact surface via bringing said contact surface into contact with a reservoir of said transfer material.

71. A method of generating a pattern on a substrate surface, said method comprising the steps of:

providing a composite patterning device comprising:

a first polymer layer comprising a three-dimensional relief pattern having at least one contact surface disposed thereon, said first polymer layer having a low Young's modulus and having a internal surface opposite said contact surface; and

a second polymer layer having an internal surface and an external surface; said second polymer layer having a high Young's modulus; wherein said first polymer layer and said second polymer layer are arranged such that a force applied to the external surface of said second polymer layer is transmitted to said first polymer layer;

contacting said composite patterning device and said substrate surface in a manner establishing conformal contact between at least a portion of said contact surface and said substrate surface, thereby generating a mold comprising the space separating said three-dimensional relief pattern and said substrate surface;

introducing a transfer material into said mold; and

separating said composite patterning device and said substrate surface, thereby generating said pattern on said substrate surface.

72. A method of generating a pattern on the surface of a substrate comprising a photosensitive material, said method comprising the steps of:

providing a composite patterning device comprising:

a first polymer layer comprising a three-dimensional relief pattern having at least one contact surface disposed thereon, said first polymer layer having a low Young's modulus and having a internal surface opposite said contact surface; and

a second polymer layer having an internal surface and an external surface; said second polymer layer having a high Young's modulus; wherein said first polymer layer and said second polymer layer are arranged such that a force applied to the external surface of said second polymer layer is transmitted to said first polymer layer;

contacting said composite patterning device and said surface of said substrate in a manner establishing conformal contact between at least a portion of said contact surface and said surface of said substrate; and

directing electromagnetic radiation through said composite patterning device and onto said surface of said substrate, thereby generating a pattern of electromagnetic radiation having a selected two-dimensional distribution of intensities on said substrate surface; wherein interaction of said electromagnetic radiation and said radiation sensitive material generates chemically modified regions of said radiation sensitive material, thereby generating said pattern on said substrate surface.

73. The method of claim 72 further comprising the step of removing at least a portion of said chemically modified regions of said substrate.

74. The method of claim 72 further comprising the step of removing at least a portion of said substrate that is not chemically modified.

75. A method of making a composite patterning device, said method comprising the steps of:

providing a master relief pattern having a selected three-dimensional relief pattern;

contacting said master relief pattern with a prepolymer of a low modulus polymer;

contacting said prepolymer material with an high modulus polymer layer;

polymerizing said prepolymer, thereby generating a low modulus polymer layer in contact with said high modulus polymer layer and in contact with said master relief pattern; said low modulus polymer layer having a three-dimensional relief pattern; and

separating said low modulus polymer layer from said master relief pattern, thereby making said composite pattering device.

76 A fiber reinforced composite patterning device for generating a pattern on a substrate surface, said device comprising:

a first polymer layer comprising a three-dimensional relief pattern having at least one contact surface disposed thereon, said first polymer layer having a low Young's modulus and having an internal surface opposite said contact surface; and

a second polymer layer having an internal surface and an external surface; said second polymer layer comprising an array of fibers in a polymer, wherein said internal surface of said second polymer layer is in contact with said external surface of said first polymer layer;

a third polymer layer having an internal surface and an external surface; said third polymer layer comprising an mesh of fibers in a polymer, wherein said internal surface of said third polymer layer is in contact with said external surface of said second polymer layer;

a fourth polymer layer having an internal surface and an external surface; said fourth polymer layer comprising an mesh of fibers in a

polymer, wherein said internal surface of said fourth polymer layer is in contact with said external surface of said third polymer layer;

a fifth polymer layer having an internal surface and an external surface; said fifth polymer layer comprising an array of fibers in a polymer, wherein said internal surface of said fifth polymer layer is in contact with said external surface of said fourth polymer layer;

wherein said composite patterning device is capable of establishing conformal contact between at least a portion of said contact surface of said first polymer layer and said substrate surface.

77. An alignment system for aligning a conformable patterning device and a substrate, said system comprising:

said conformable patterning device comprising a first polymer layer having a contact surface with a first alignment element, said first polymer layer having a low Young's modulus, said first alignment element comprising either a recessed region or a relief feature;

said substrate having an external surface; wherein said external surface comprises a second alignment element comprising either a recessed region or a relief feature that is complementary to said first alignment element;

a patterning agent present between said contact surface of said conformable patterning device and said external surface of said substrate;

wherein said contact surface is capable of establishing conformal contact with said external surface such that said first and second alignment features engage.

78. The system of claim 77 wherein said conformable patterning device further comprises additional relief features, recessed regions or both relief features and recessed regions, wherein conformal contact of said contact surface and said external surface generates spaces occupied by said patterning agent.

79. The system of claim 78 wherein said patterning agent absorbs, scatters or reflects electromagnetic radiation directed onto said conformable patterning device, thereby generating electromagnetic radiation having a selected two dimensional spatial distribution of intensities that is transmitted to said external surface.

80. The system of claim 77 wherein said patterning agent is a lubricant capable of lowering the friction between said contact surface and said external surface of said substrate.

81. The system of claim 77 wherein said first and second alignment elements are relief features or recessed regions having shapes selected from the group consisting of pyramidal, cylindrical, polygonal, triangular, rectangular, square, conical, trapezoidal and spherical.

82. The system of claim 77 wherein the conformable patterning device is a composite patterning device further comprising one or more additional polymer layers connected to said first polymer layer.

83. A method of aligning a conformable patterning device and a substrate, said method comprising:

providing said conformable patterning device comprising a first polymer layer having a contact surface with a first alignment element, said first polymer layer having a low Young's modulus, said first alignment element comprising either a recessed region or a relief feature;

providing said substrate having an external surface; wherein said external surface comprises a second alignment element comprising either a recessed region or a relief feature that is complementary to said first alignment element;

providing a patterning agent between said contact surface of said conformable patterning device and said external surface of said substrate; and

establishing conformal contact between said contact surface and said external surface such that said first and second alignment features engage.

84. The method of claim 83 wherein said patterning agent is a lubricant capable of lowering the friction between said contact surface and said external surface of said substrate.

Fig. 1A

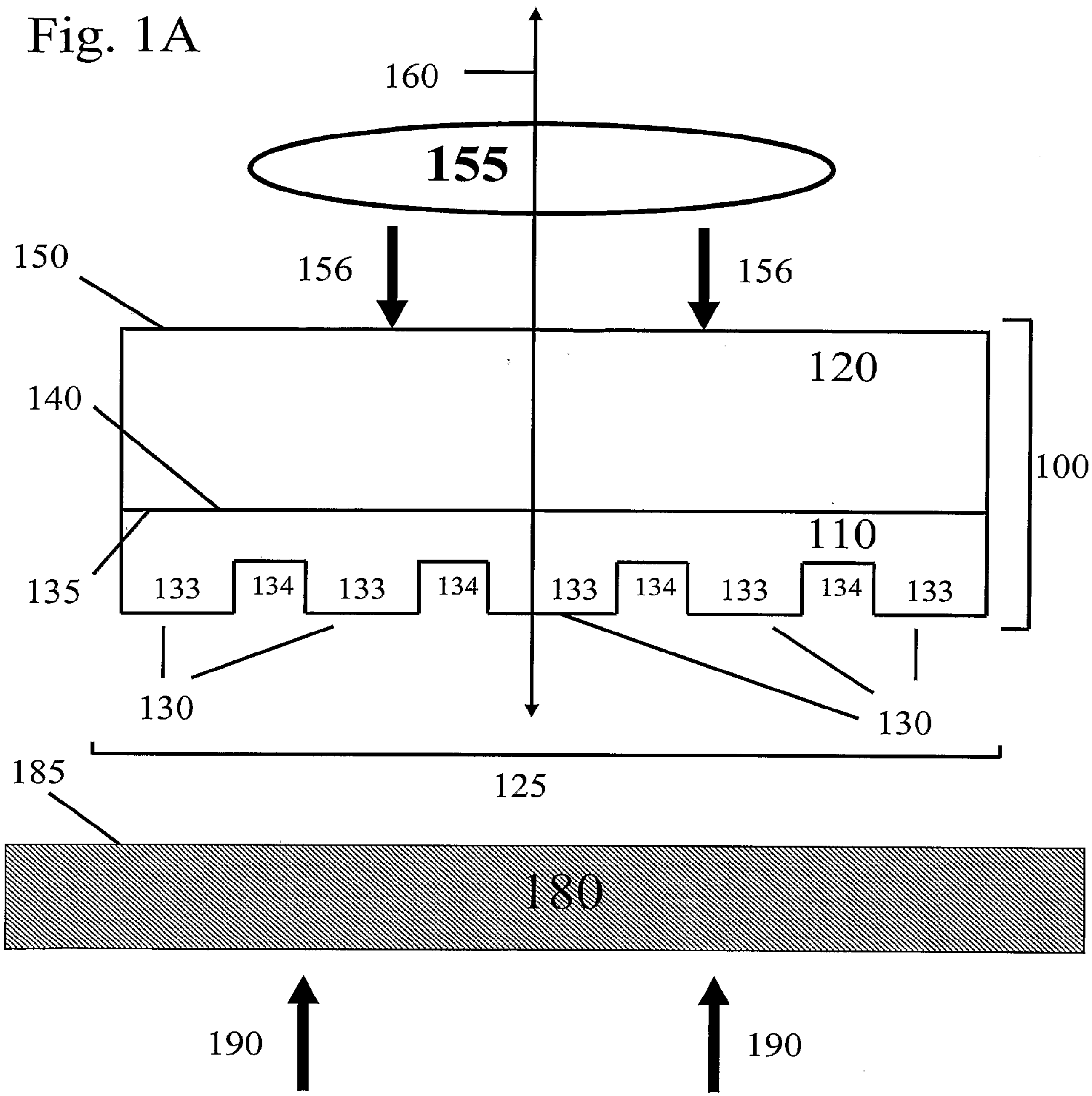

160
155
150
156
156
120
140
100
110
135
133
134
133
134
133
134
133
134
133
130
130
125
185
180
190
190

Fig. 1B

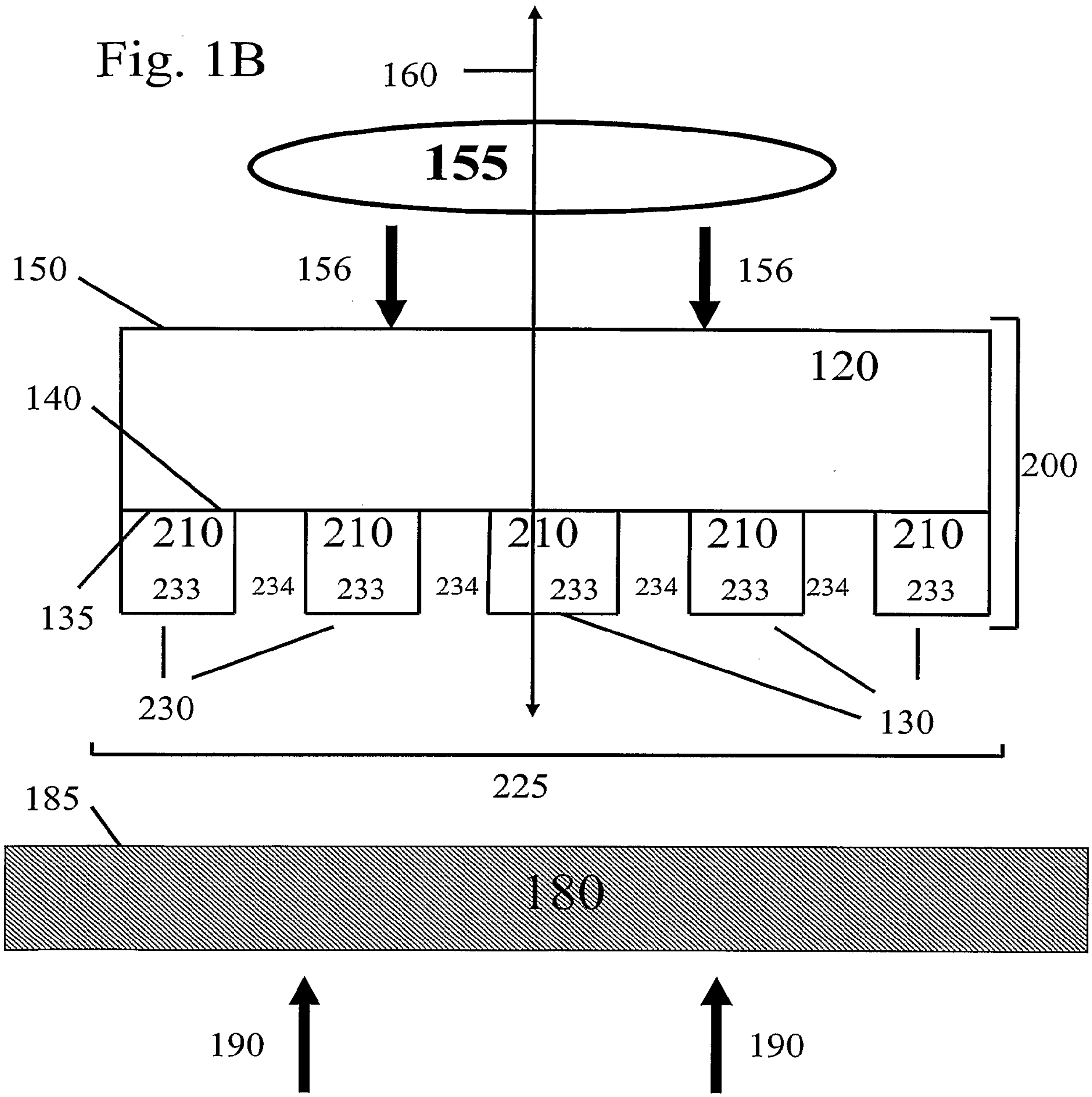

160
155
150
156
156
120
140
200
210
210
210
210
210
233
234
233
234
233
234
233
234
233
135
230
130
225
185
180
190
190

Fig. 1C

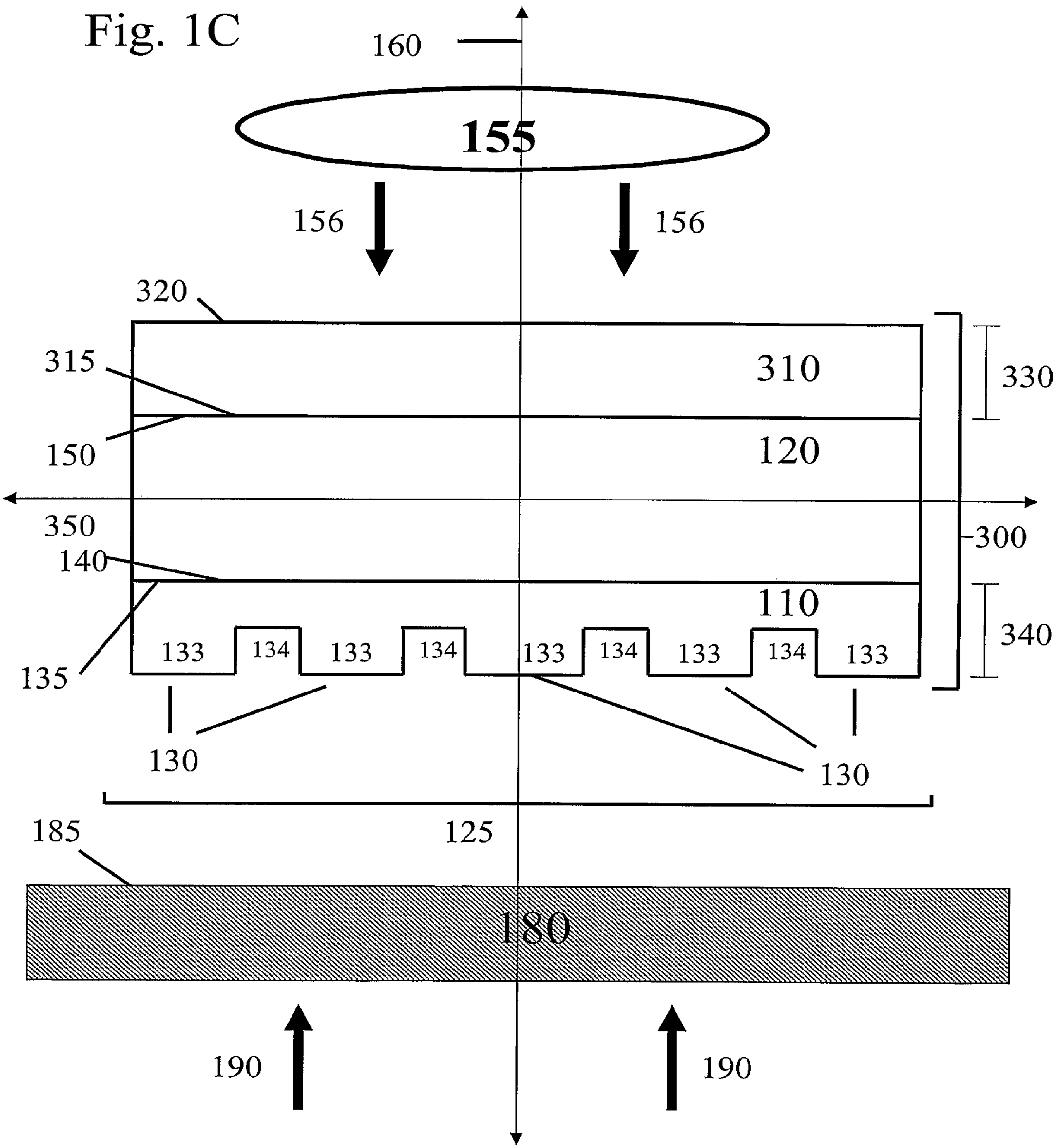

160
155
156
156
320
315
310
330
150
120
350
300
140
110
340
133
134
133
134
133
134
133
134
133
135
130
130
125
185
180
190
190

Fig. 1D

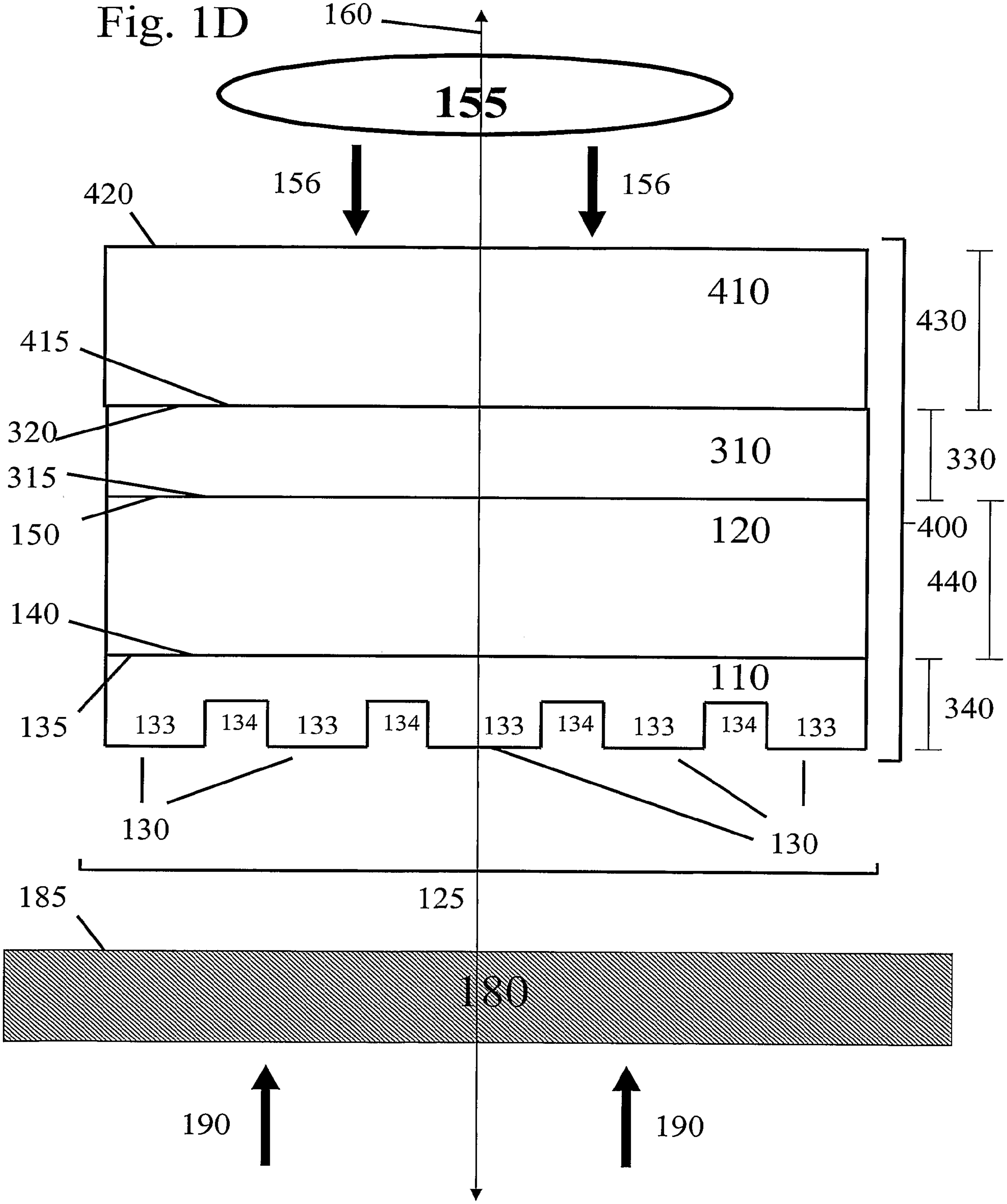

160
155
156
156
420
410
430
415
320
310
330
315
150
120
400
440
140
110
340
135
133
134
133
134
133
134
133
134
133
130
130
125
185
180
190
190

Fig. 2A

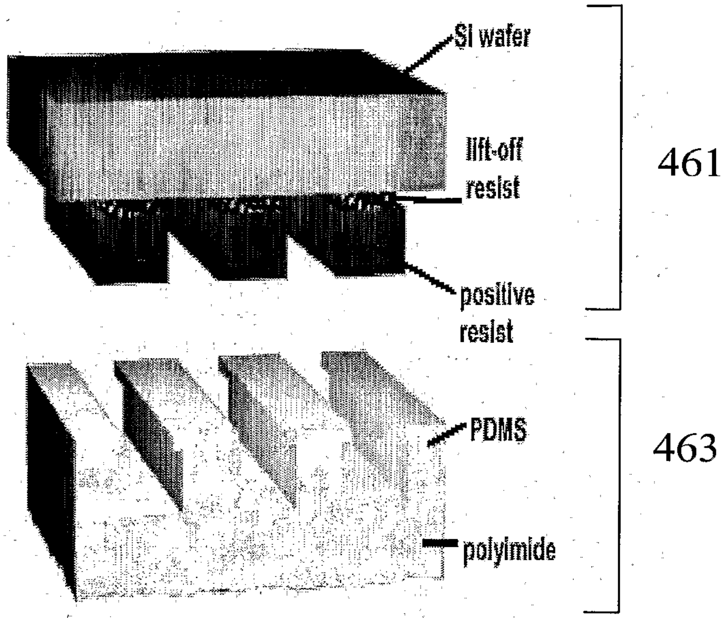

Si wafer
lift-off resist
positive resist
461
PDMS
polyimide
463

Fig. 2B

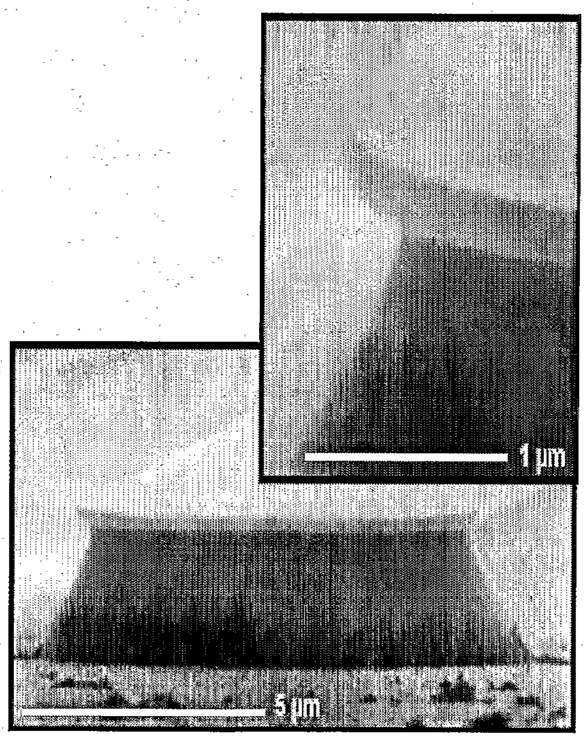
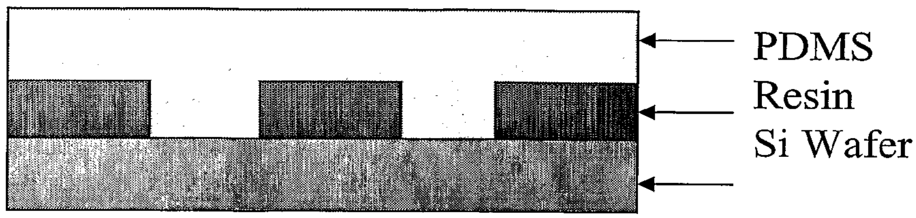

1 μm
5 μm

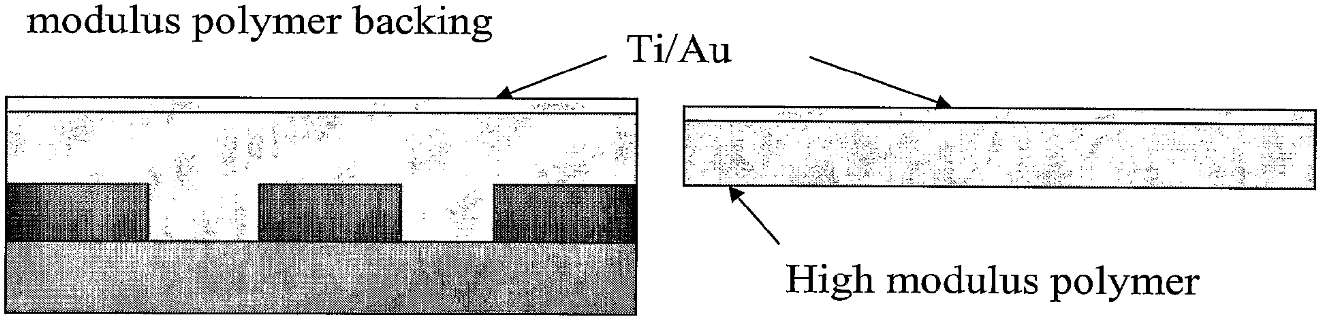
Fig. 3A

a) Spin coating of low modulus elastomeric material (3000~6000 RPM)

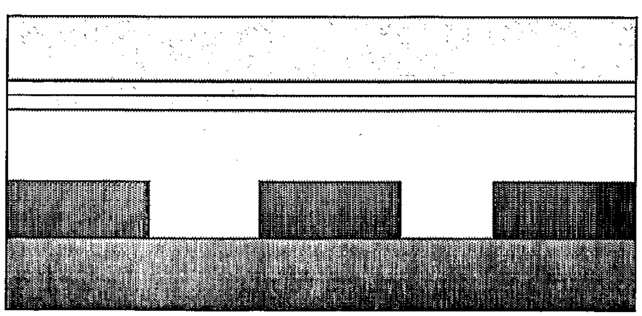


b) Oven/hot plate curing of the elastomeric material (few hours at 60~80°C for PDMS)

c) e-beam evaporation of Ti/Au on eleastomeric material and high modulus polymer backing



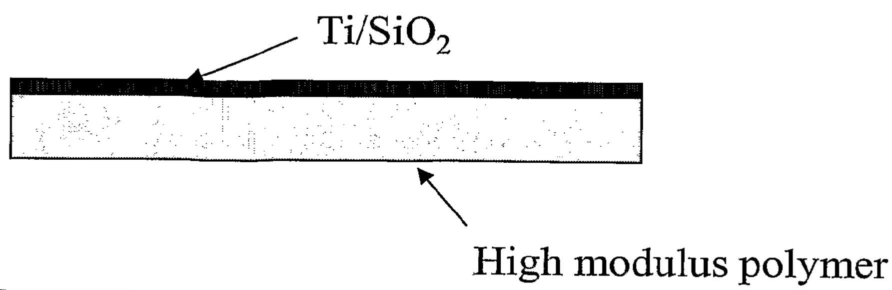
d) Cold welding of the high modulus polymer on top of the low modulus elastomeric material



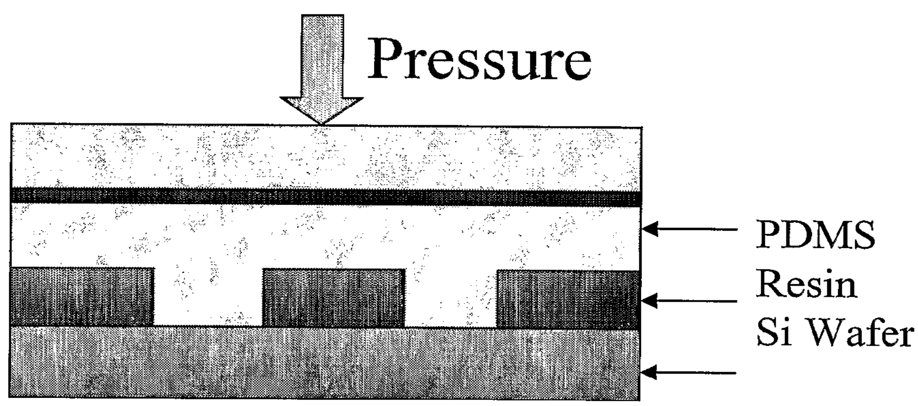
e) The composite stamp is pealed away from the master

Fig. 3B

a) e-beam evaporation of Ti/SiO_2 on a high modulus polymer backing



b) The Ti/SiO_2 primed high modulus polymer is brought into contact with a PDMS coated master



The thickness of the PDMS layer can be reduces to a desired value by:
-spinning the master with the high modulus polymer lying on top
-applying pressure on the back of the high modulus polymer with a flat or rocker based press

c) Oven curing of the elastomeric material (few hours at 60~80°C for PDMS)

d) The composite stamp is pealed away from the master

Fig. 4A

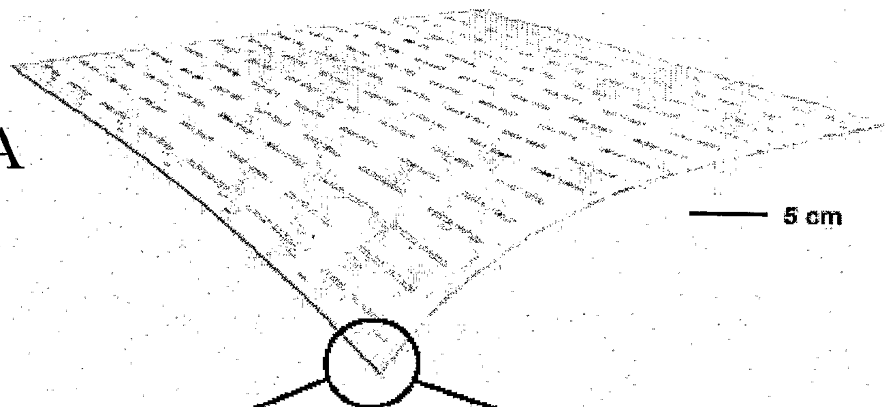


Fig 4B

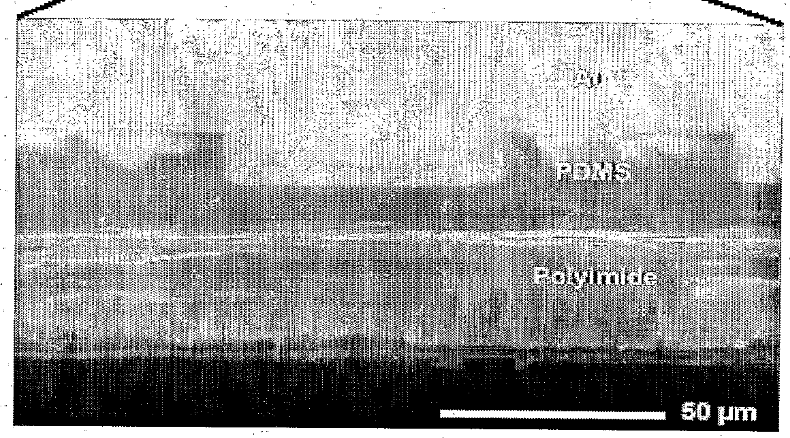


Fig. 5A

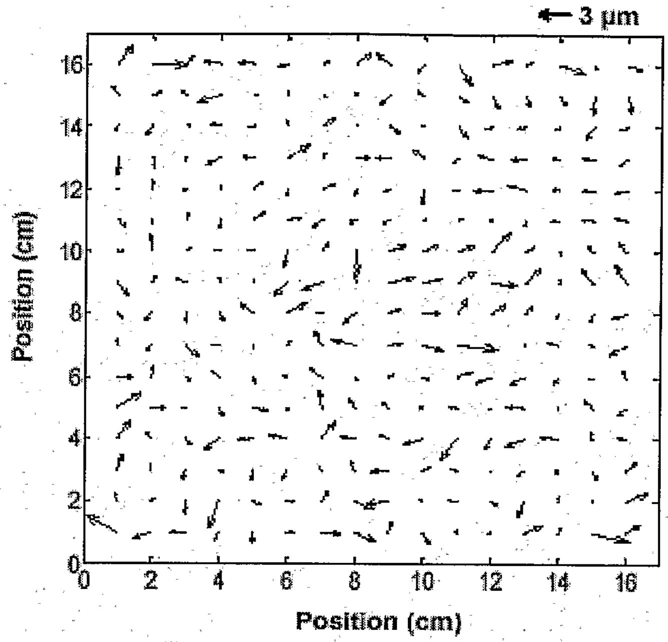

3 µm
Position (cm)
Position (cm)
0
2
4
6
8
10
12
14
16

Fig. 5B

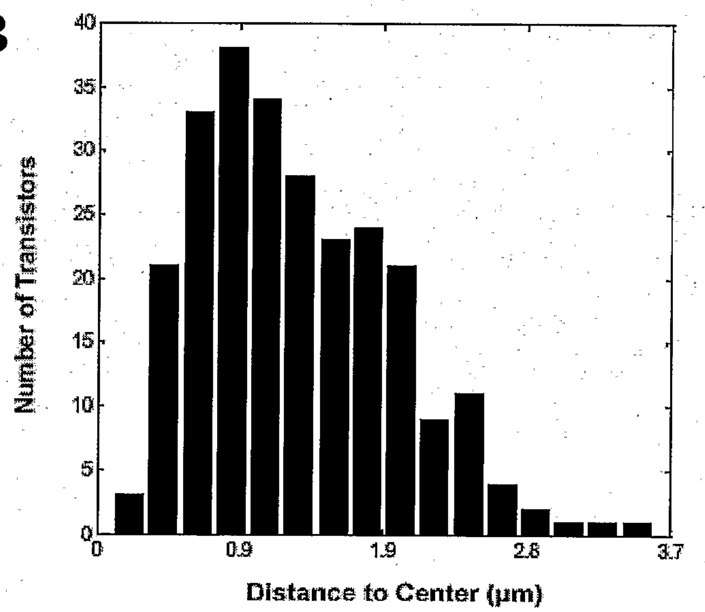

Number of Transistors
Distance to Center (µm)
0
5
10
15
20
25
30
35
40
0.9
1.9
2.8
3.7

Fig. 6A

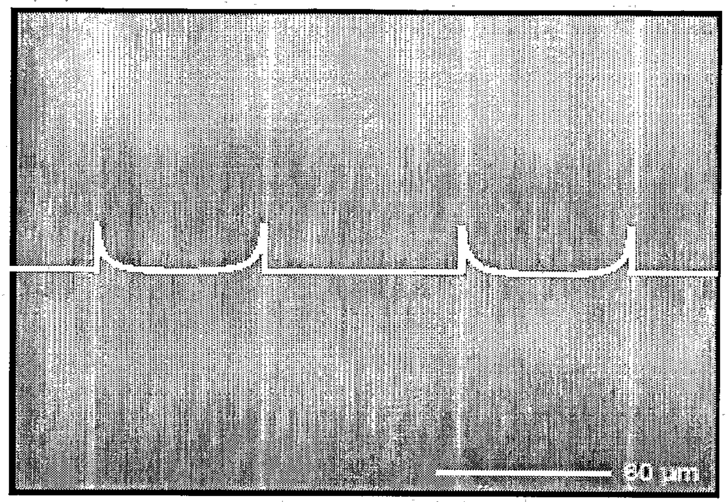


Fig. 6B

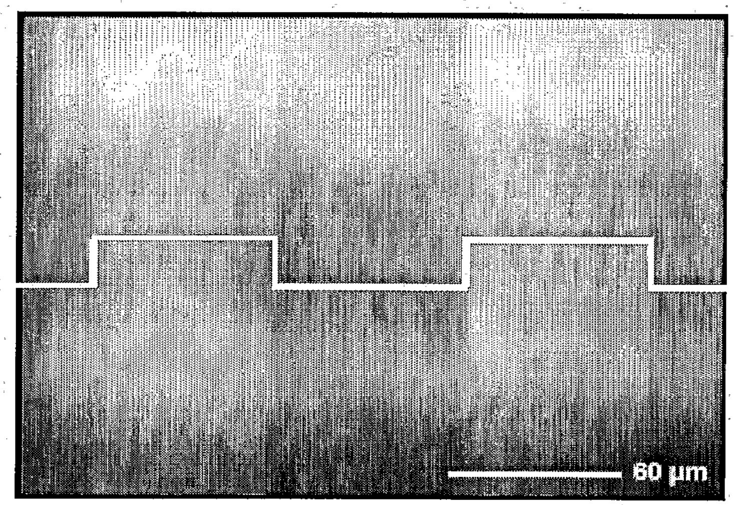
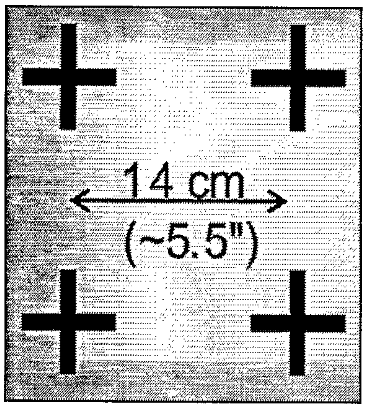
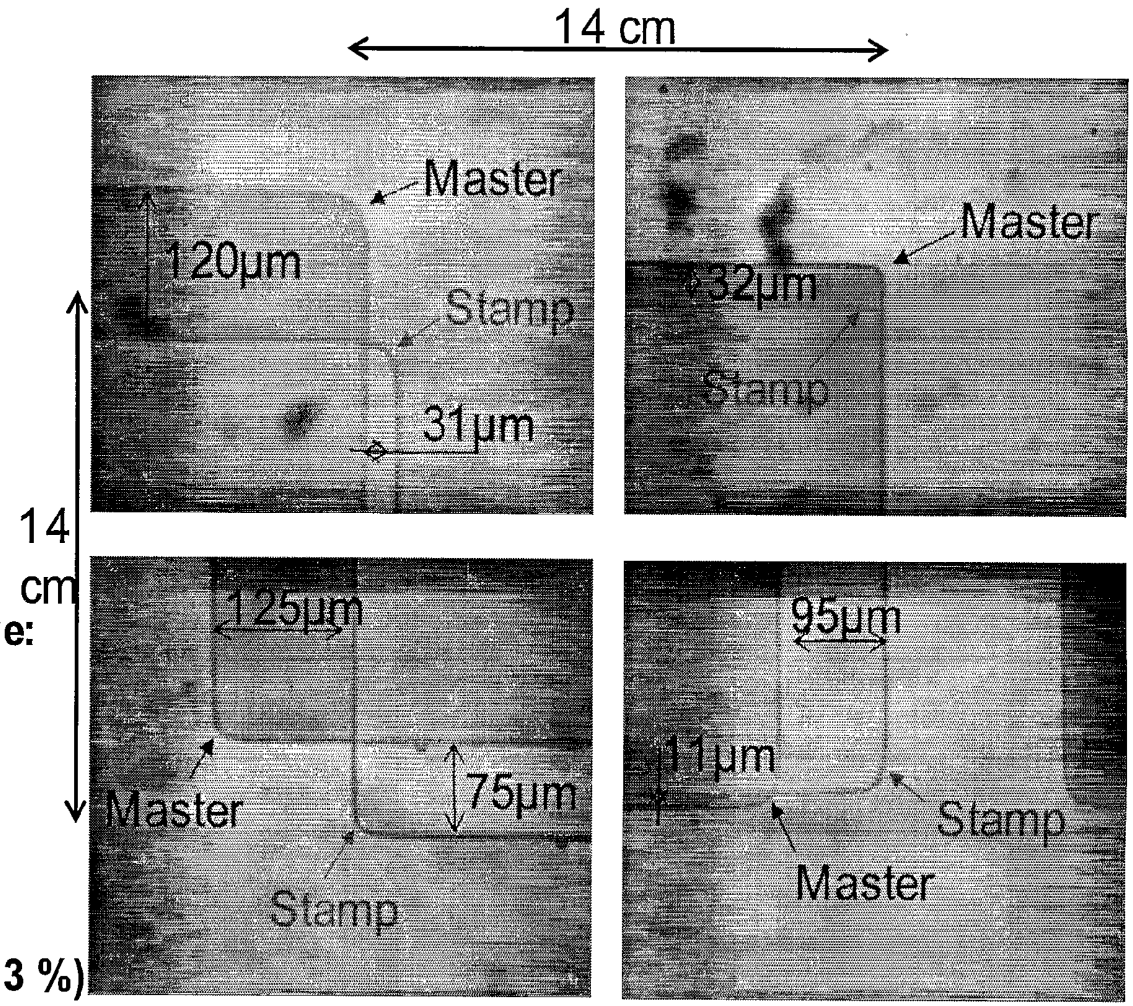


Fig. 7 Shrinkage of the Kapton stamp

Alignment marks





Horizontal shrinkage:

Δx ~ 0.2 %

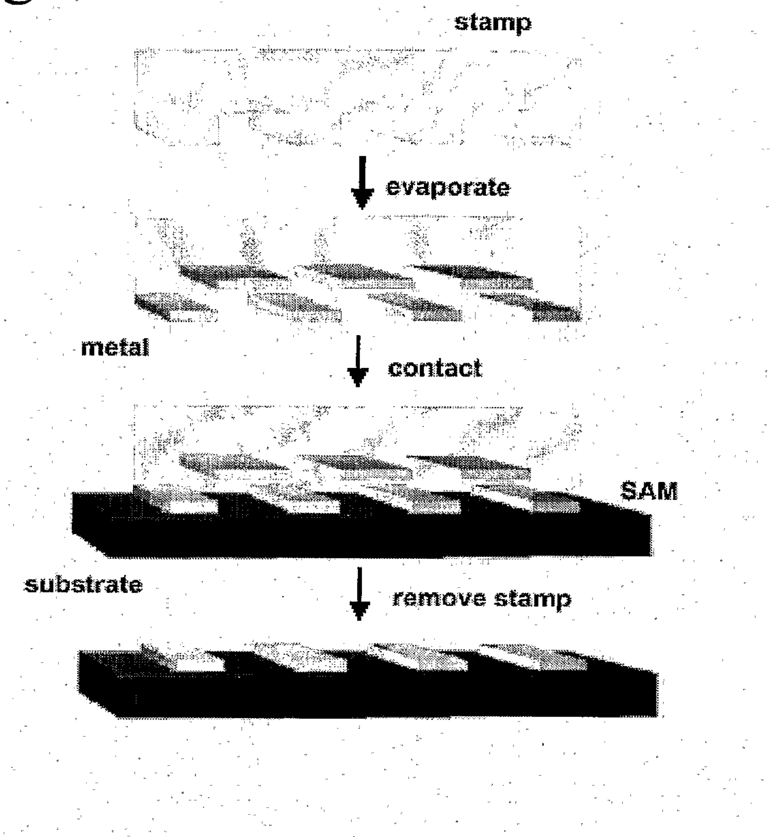
Vertical shrinkage:

Δy ~ 0.3 %

(Thick PDMS ~ 2 to 3 %)

εx ~ 30 µm, εy ~ 45 µm

Fig. 8



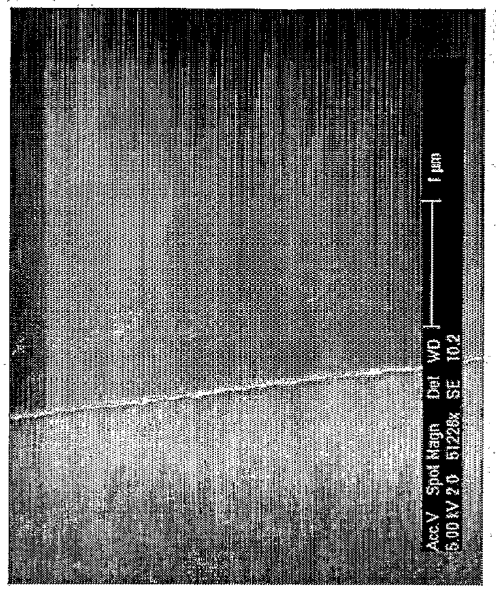


Fig. 9C

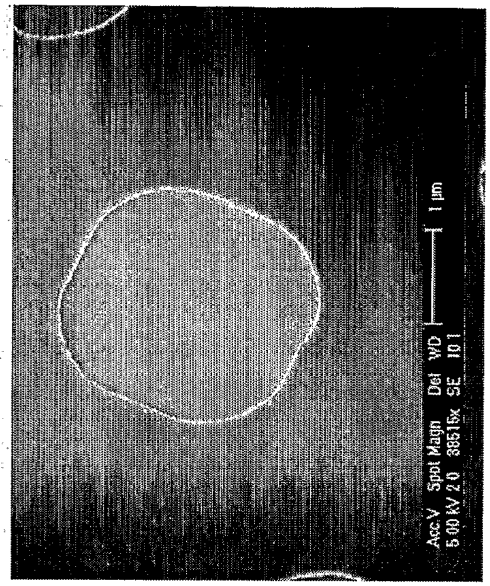


Fig. 9D

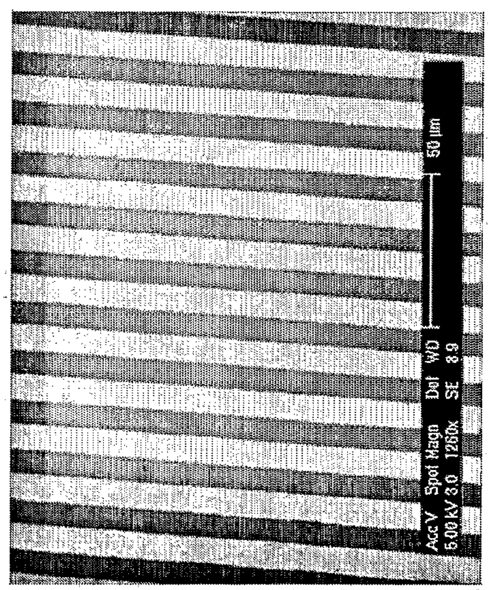


Fig. 9A

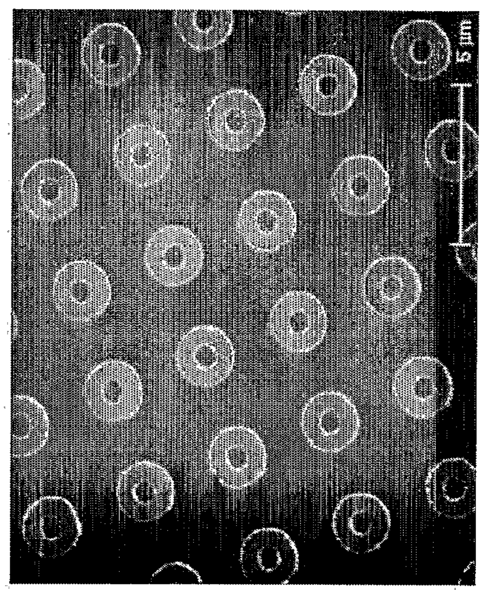
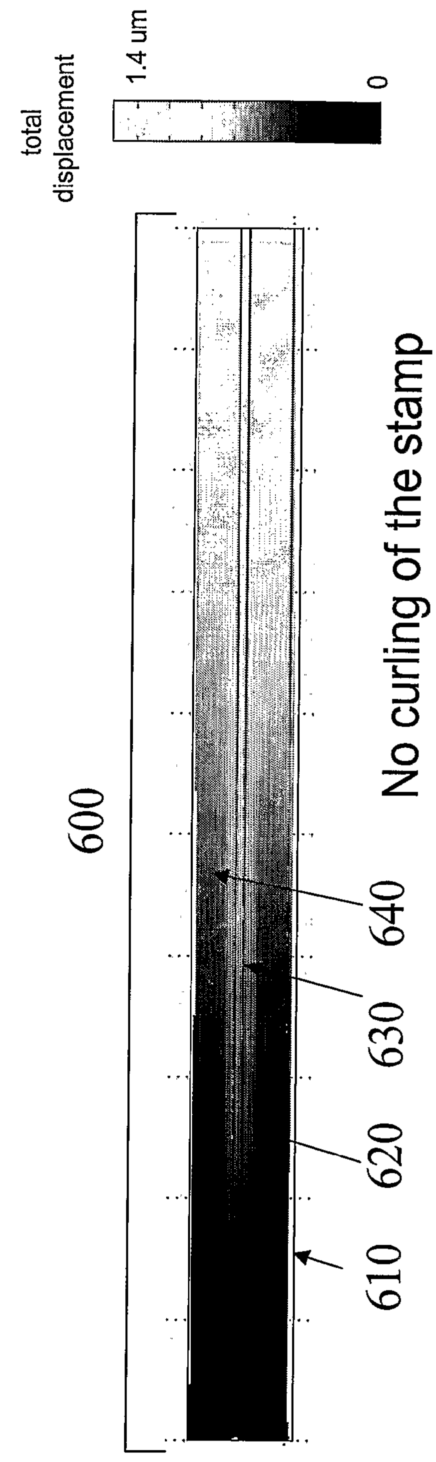


Fig. 9B

Fig. 10



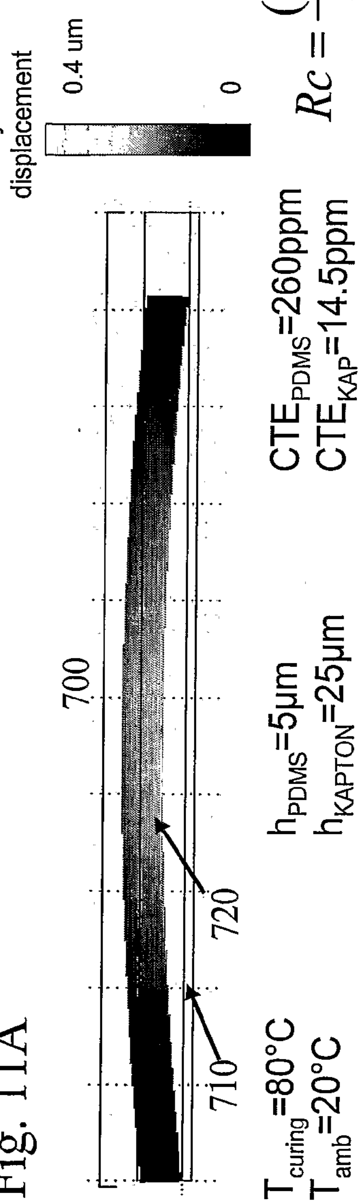
T_{curing}=80°C
T_{amb}=20°C

h_{PDMS}=5μm
h_{KAPTON}=25μm

CTE_{PDMS}=260ppm
CTE_{KAP}=14.5ppm

E_{PDMS}=3MPa
E_{KAP}=5.34GPa

Fig. 11A



$$Rc = \frac{(x'^2 + y'^2)^{3/2}}{x'.y'' - y'.x''}$$

Fig. 11B

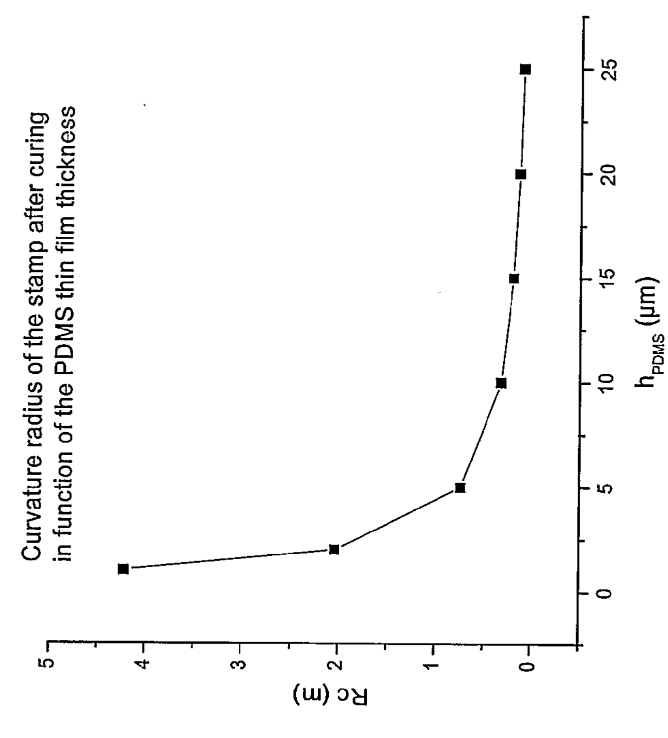


Fig. 11C

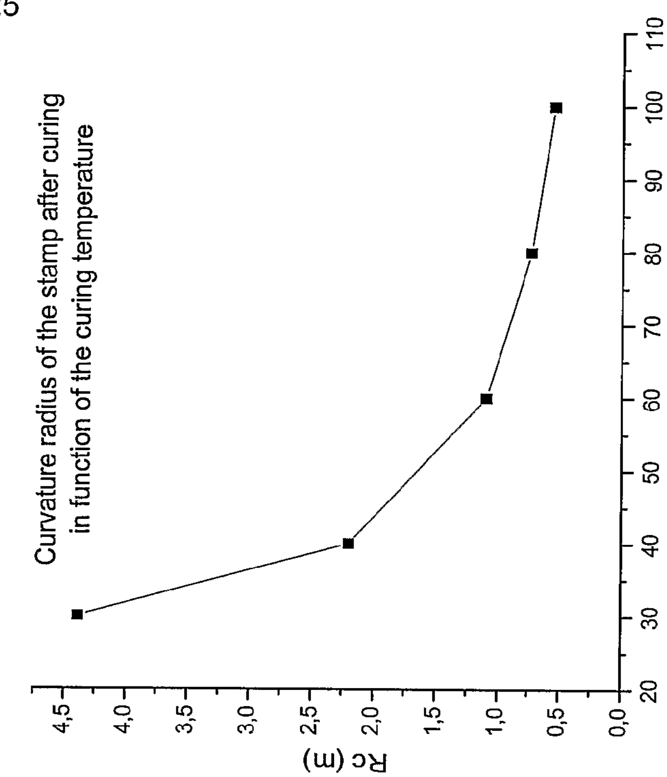


Fig. 12A Weight driven sagging of a double kapton backed stamp

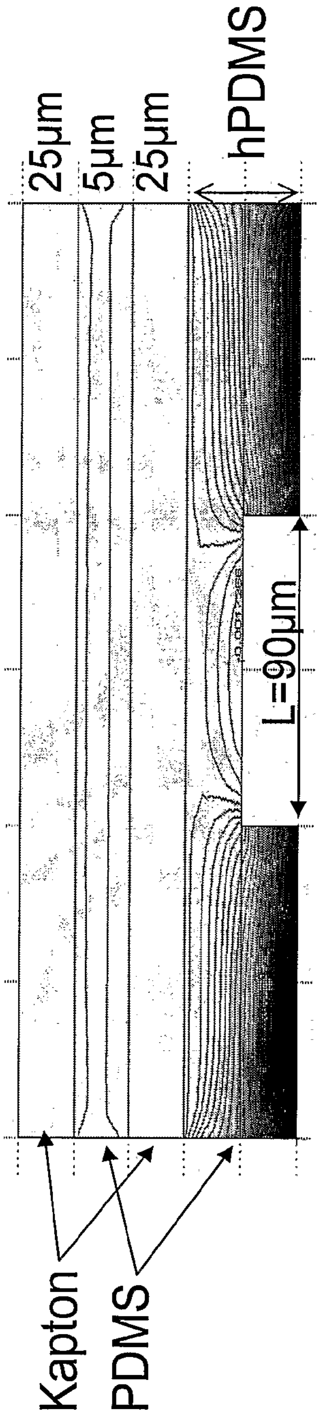


Fig. 12B

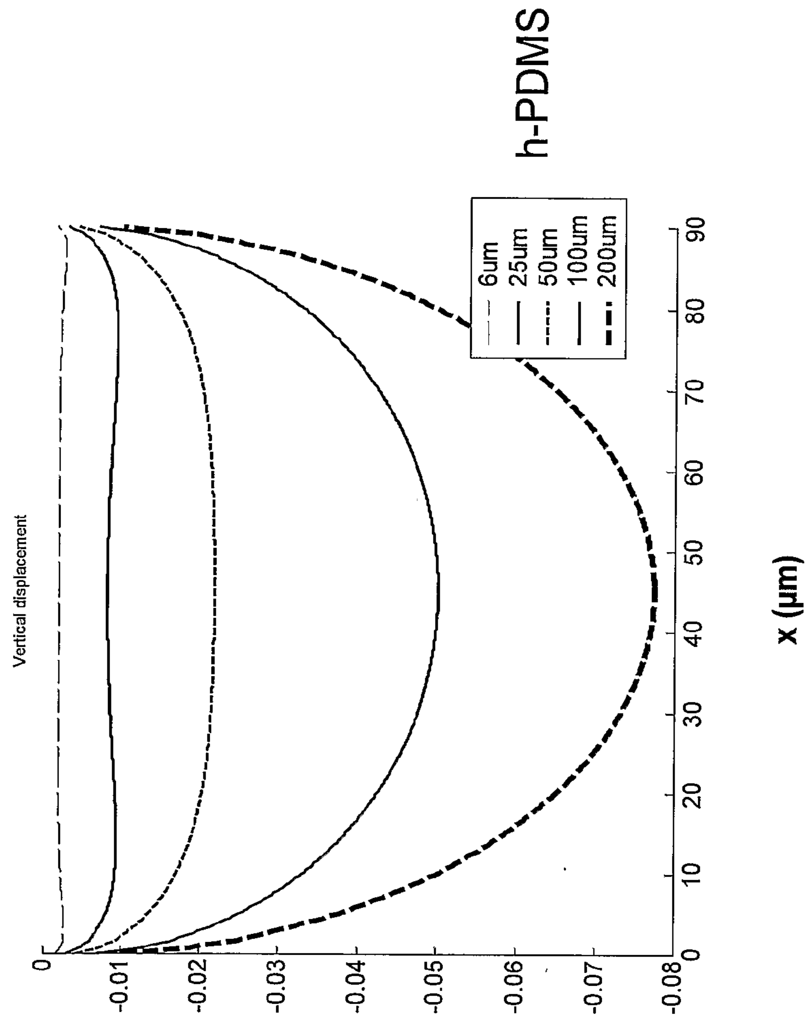


Fig. 13A

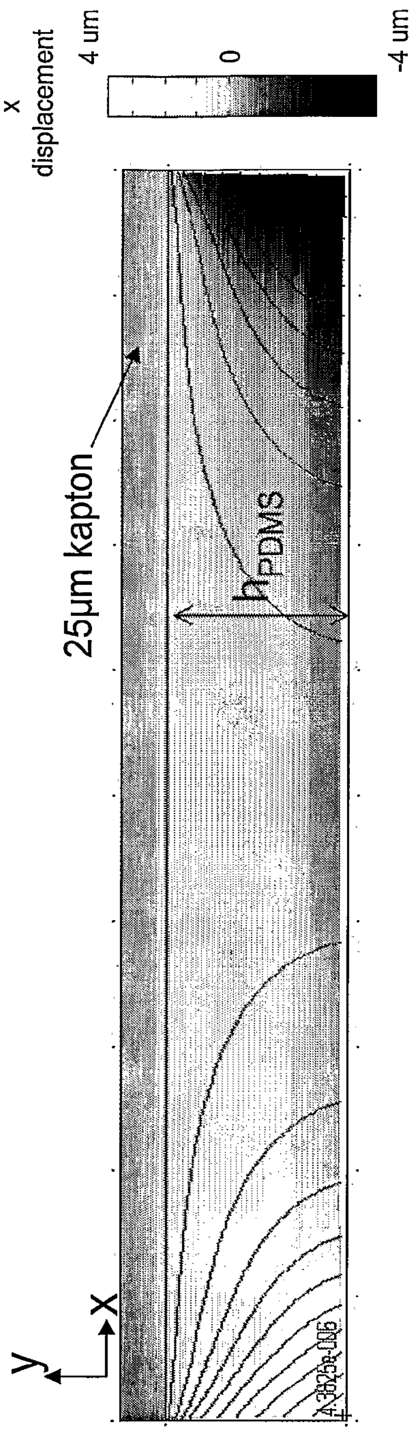


Fig. 13C

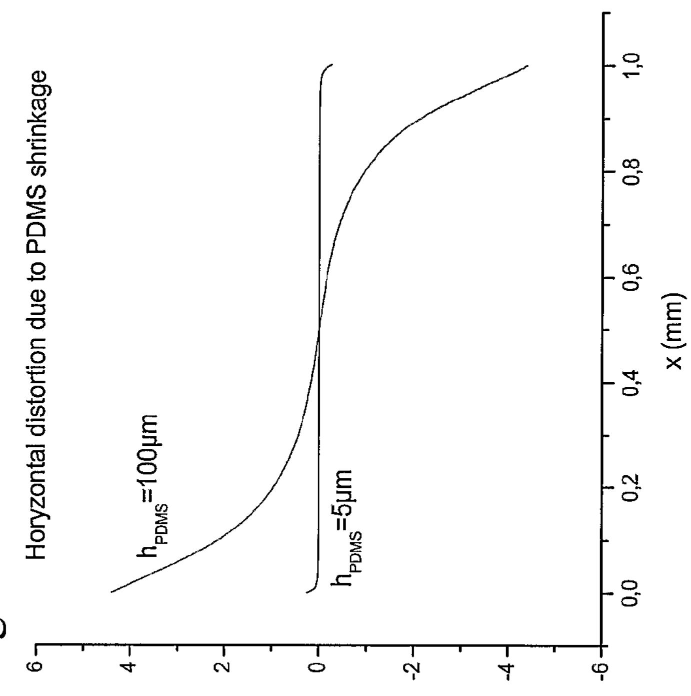
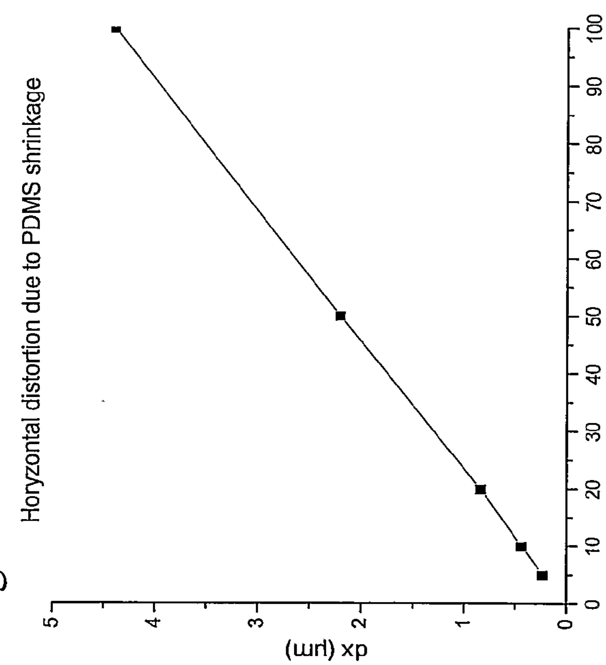


Fig. 13B



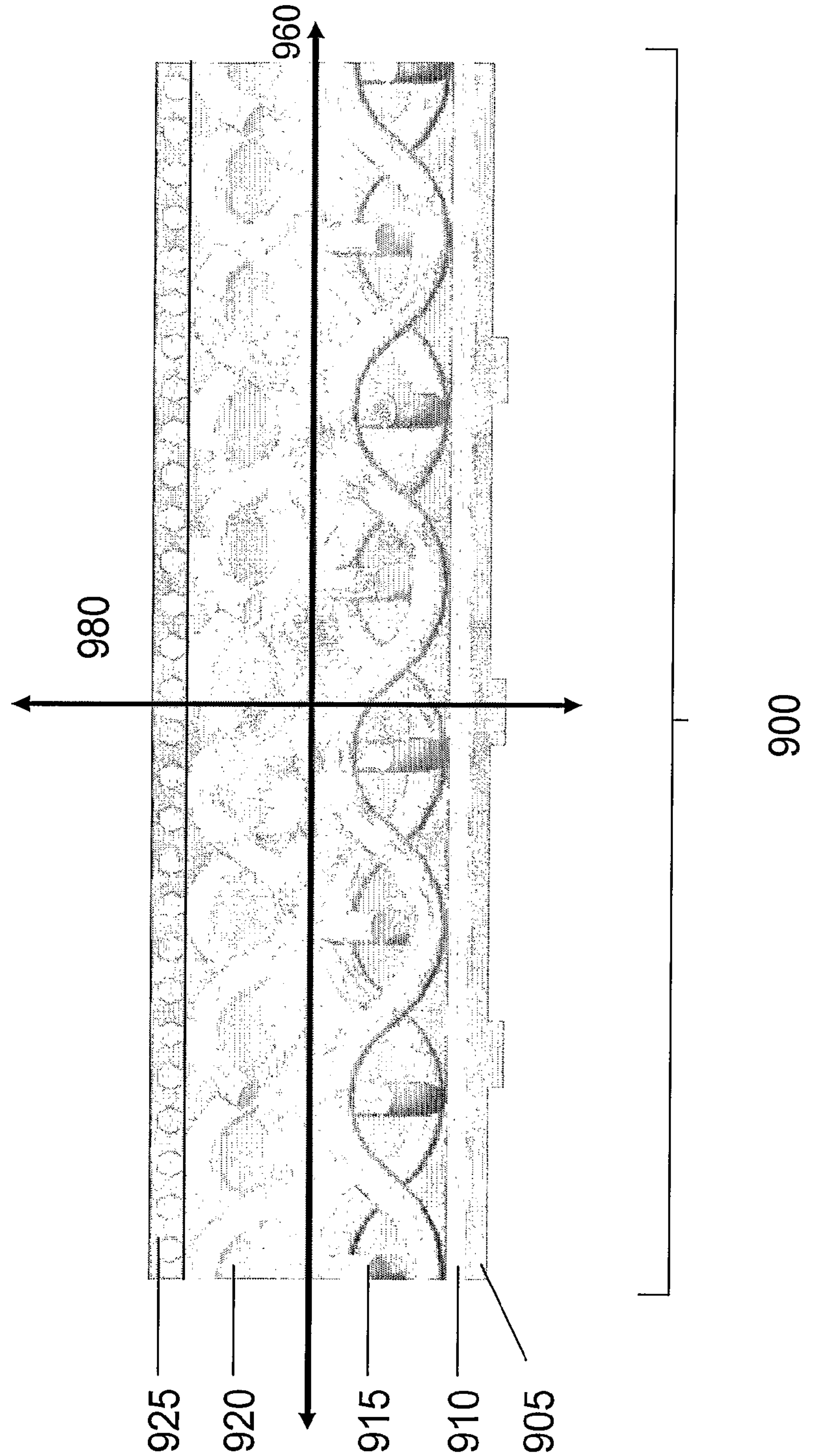


Fig. 14 A

Fig. 14B

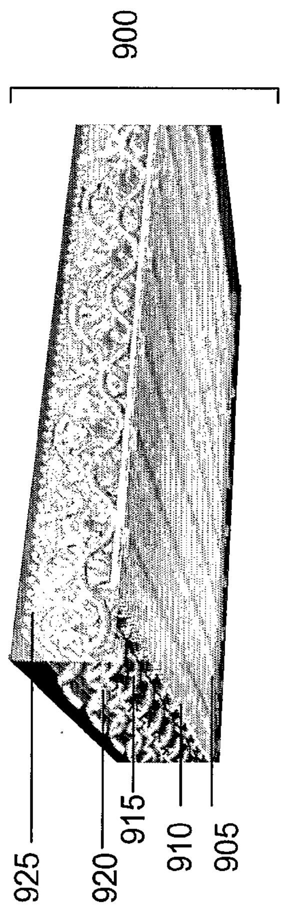
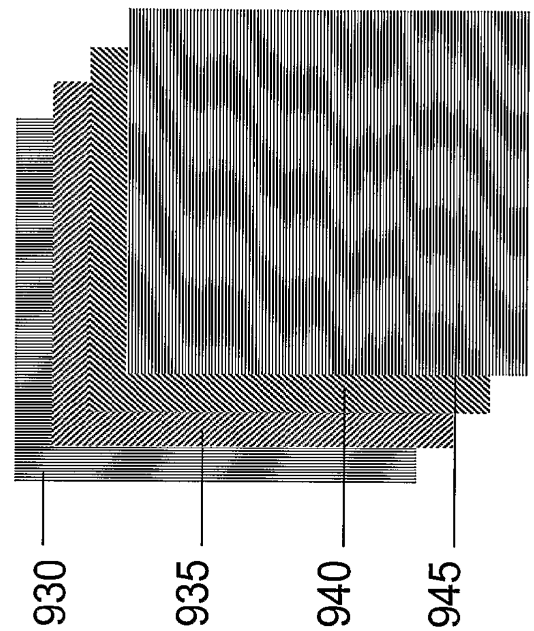


Fig. 14C



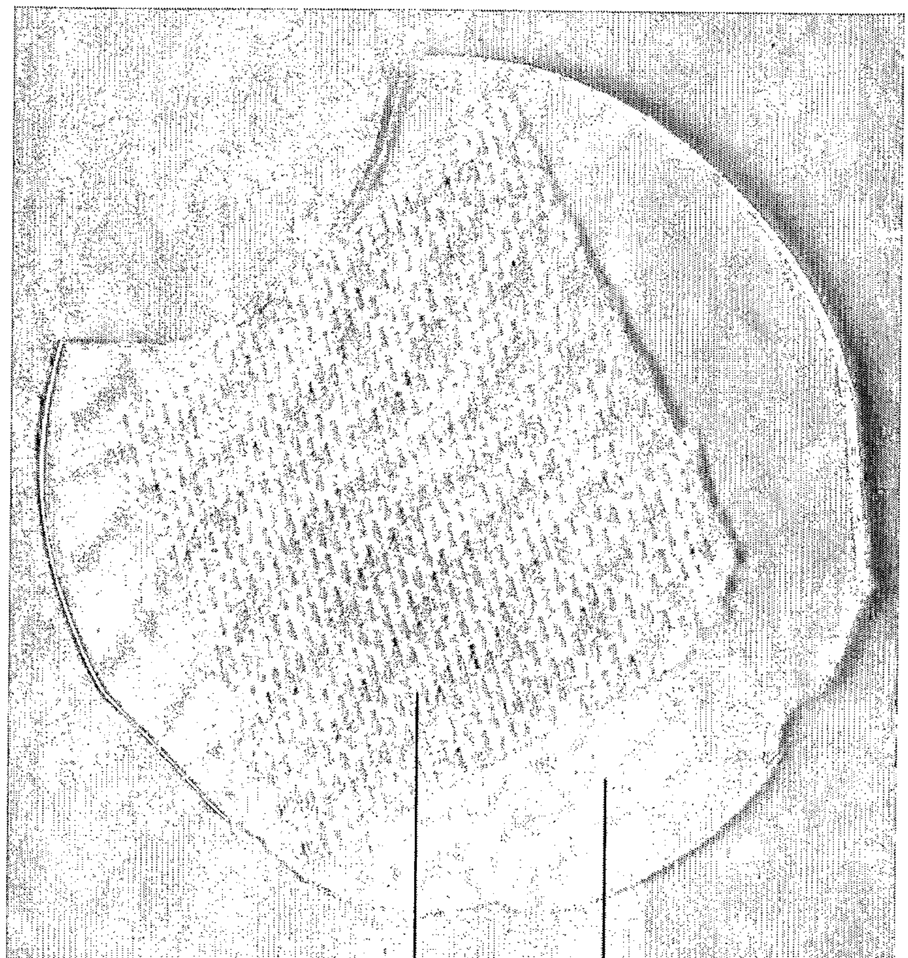


Fig. 15

971

972

Fig. 16

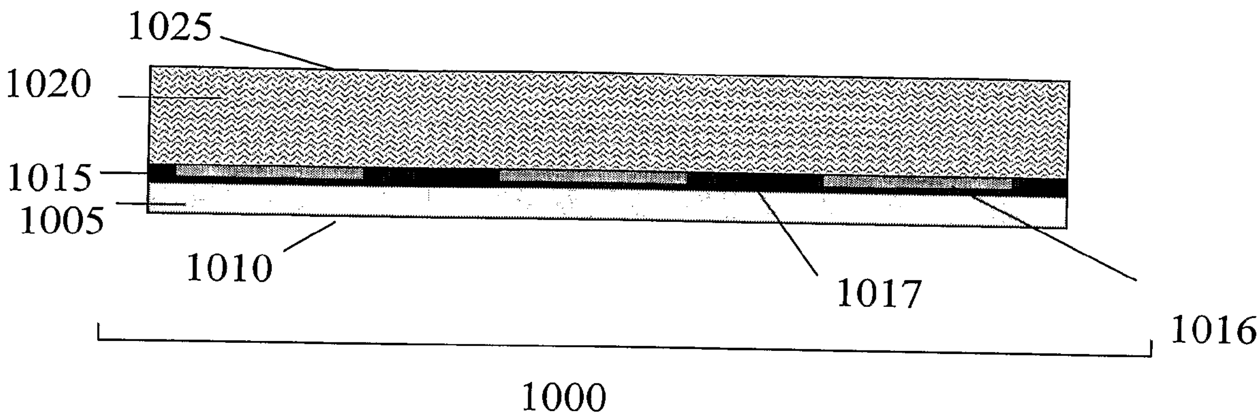


Fig. 17A

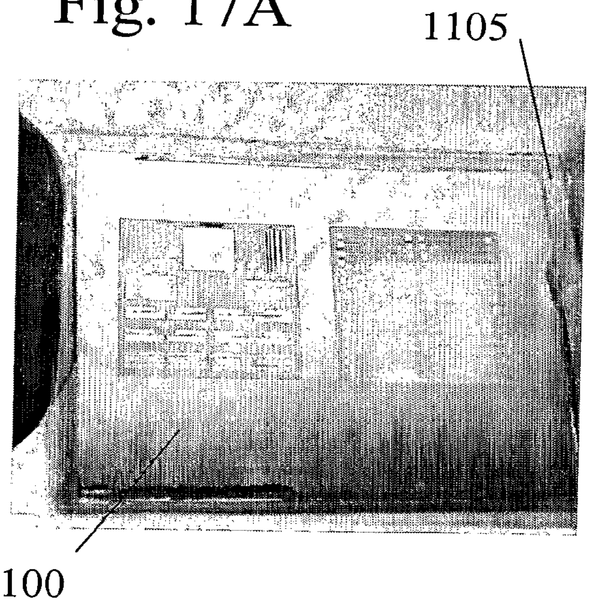


Fig. 17B

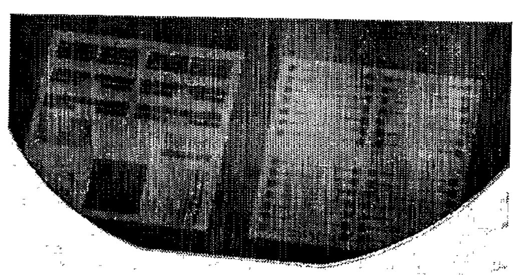
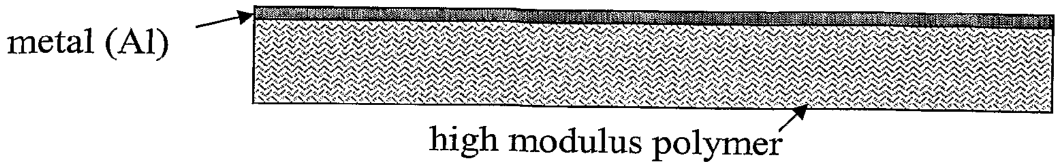
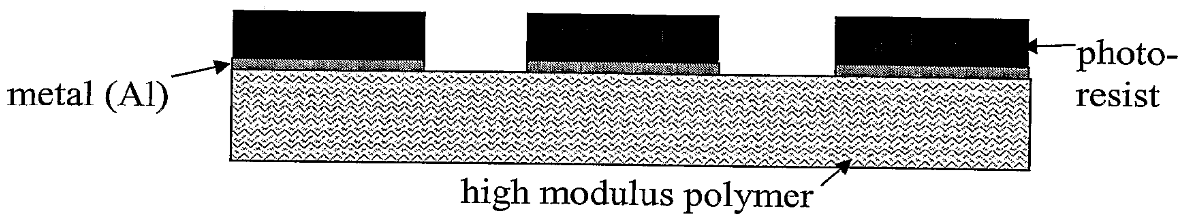


Fig. 18

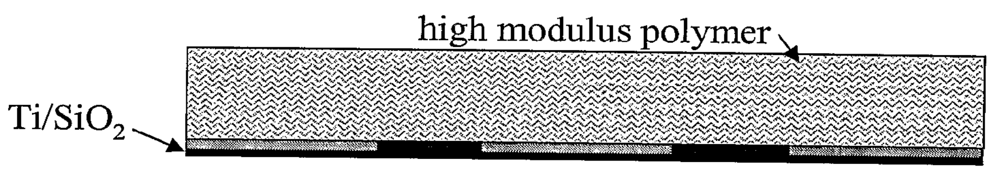
A: e-beam evaporation of metal (Al) on a high modulus polymer backing



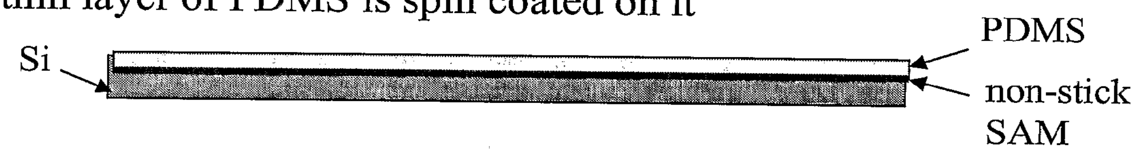
B: photo-lithography and back solution etching of the metal layer



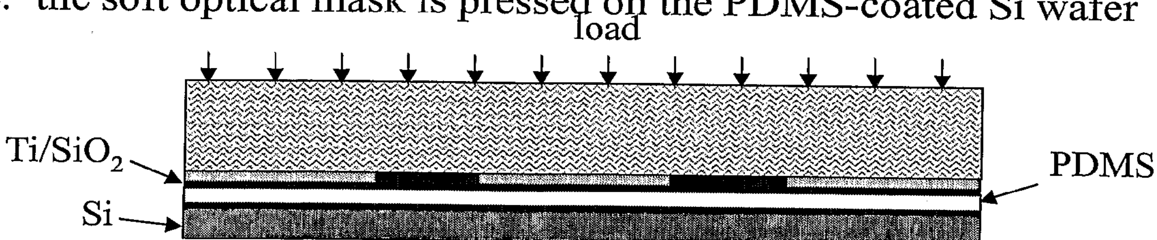
C: e-beam evaporation of Ti/SiO_2 to promote adhesion of the PDMS



D: a flat Si substrate is treated with a non-stick SAM and then a thin layer of PDMS is spin coated on it



E: the soft optical mask is pressed on the PDMS-coated Si wafer



F: oven curing of the elastomeric material (few hours at 60~80°C for PDMS)

G: the soft optical mask is pealed away from the master

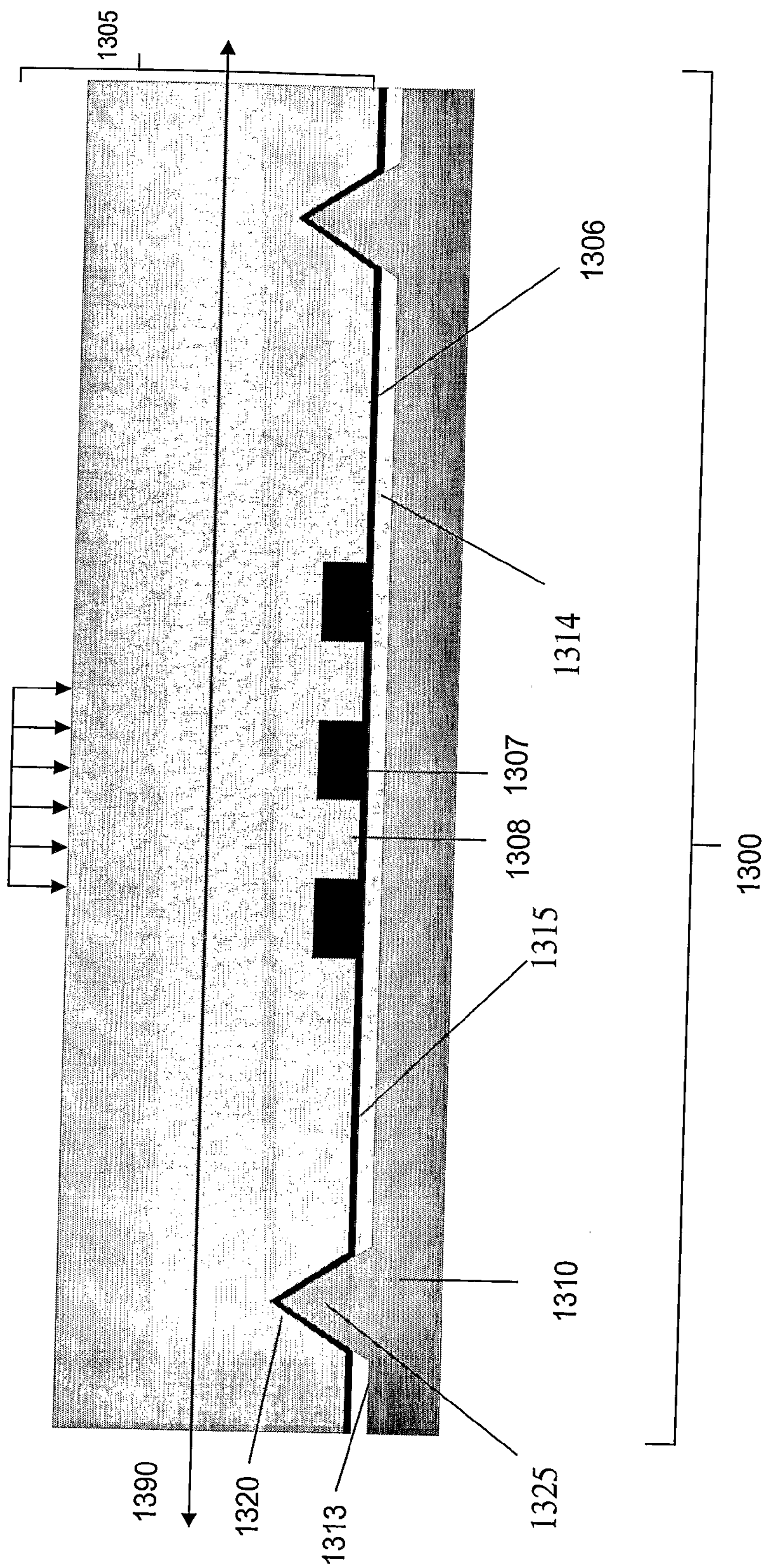

1305
1306
1314
1380
1307
1308
1300
1315
1310
1390
1320
1313
1325

Fig. 19A

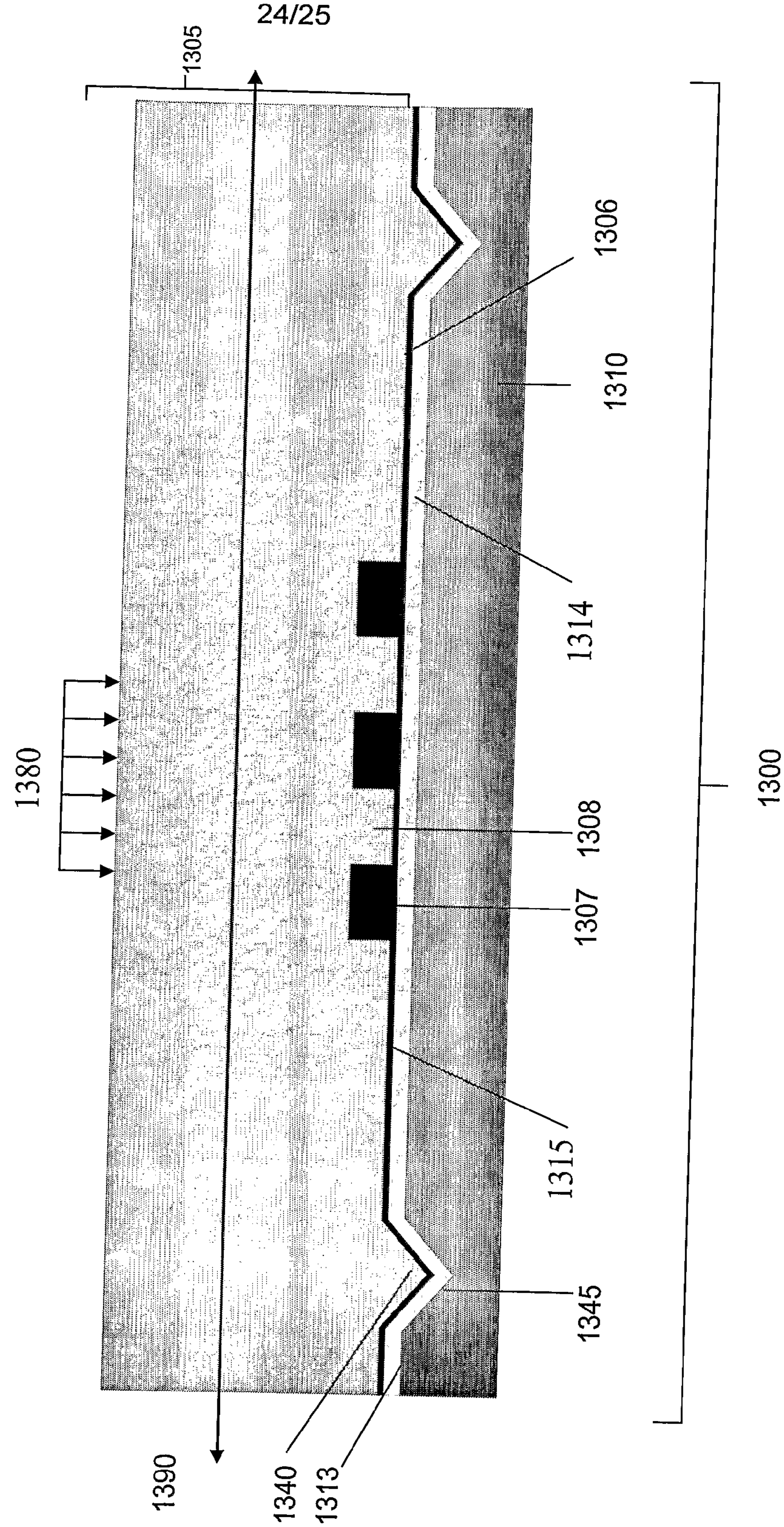
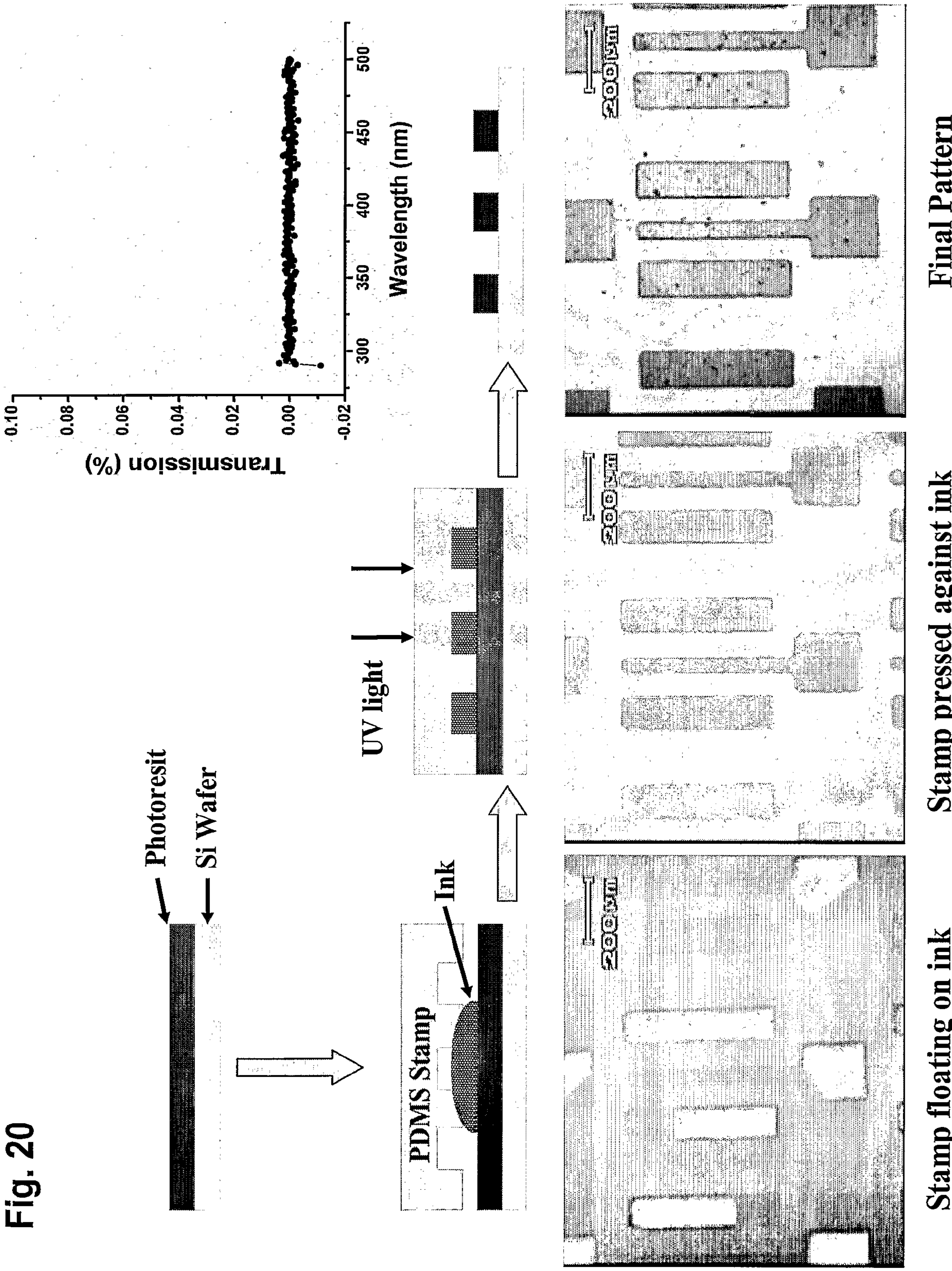

1305
1306
1310
1314
1380
1300
1308
1307
1315
1345
1390
1340
1313

Fig. 19B

Fig. 20


Photoresit
Si Wafer
PDMS Stamp
Ink
UV light
Transmission (%)
0.10
0.08
0.06
0.04
0.02
0.00
-0.02
300
350
400
450
500
Wavelength (nm)
200 µm
Stamp floating on ink
Stamp pressed against ink
Final Pattern